Climate and Land Use Change Impacts on N-Loads in Iowa Rivers and Remediation of Tile Water with an Anion-Exchange Resin

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ABSTRACT

This research was conducted to (1) better understand the underlying reasons for a continuous increase in nitrate loads in the Gulf of Mexico, and (2) if an industrial anion resin can be used at a field scale to reduce N losses from tile-drained watersheds to the rivers. The first objective was accomplished through statistical analyses of climate and land use change impacts on streamflow, baseflow, flow weighted nitrate-N concentrations (FWNC) and nitrate-N-loads in three major rivers of Iowa. The rivers included the Des Moines River, the Iowa River, and the Raccoon River. The results from this analysis showed that natural log of annual streamflow, baseflow, and N-loads were primarily controlled by the precipitation in the corresponding watersheds. For streamflow and baseflow, this precipitation corresponded to the current years as well as previous year precipitation. Previous year precipitation reflected the lack or excess presence of stored water in the soil and its consequences in terms of increased or decreased overland flow, infiltration, and percolation processes. For N loads, the precipitation effect was limited to one-year precipitation for the Des Moines and the Iowa Rivers and two-year precipitation for the Raccoon River. There were individual years when streamflow, baseflow, and N loads were impacted by up to three previous years' precipitation. Effect of land use change, in terms of increased soybean area, had no effect on annual streamflow, annual baseflow, annual flow-weighted N concentrations or annual N-loads in all three rivers. Additional regression analysis of FWNC and N-loads from 1987-2001 showed no effect of N fertilizer use as an explanatory variable for any of the three watersheds.

Statistical analysis of the combined annual data from all three rivers showed that there was a unique relationship between the natural log of streamflow, the baseflow, and the N-yield (N-loads/watershed area) versus the precipitation. The precipitation effects were both in terms of current year precipitation and the previous year precipitation. The coefficient of determination (R^2) of Ln(streamflow), Ln(baseflow) and Ln(N load) with precipitation for the combined data were 0.74, 0.70 and 0.54, respectively. Limited scatter in the N-yield data at a given annual precipitation level over three rivers suggested that variation in annual precipitation has much bigger impact on N losses than the differences in cultural or cropping practices between the three river watersheds over the study period. Considering that there has been a 10-15% increase in precipitation in the Upper Midwestern United States in recent years, the combined N Yield relationship with precipitation would suggest that the recent increases in N-loads or increased hypoxic area in the Gulf of Mexico are likely due to increased precipitation. Statistical analysis of N-loads over a shorter period of time (1987-2001) also showed that changes in fertilizer use had no effect on river N-loads.

Regression analysis of monthly streamflow, baseflow, N-loads and FWNC concentration showed that natural log of streamflow, baseflow, and N-loads were generally linearly related to precipitation in a given month and a few prior months. In some cases earlier in the season, these variables were also related to previous year's precipitation, an indication that some of the past water stored in the soil both above and below the drain tile is interacting with current months precipitation and affecting the streamflow and baseflow. In most cases, there was no effect of soybean area on natural log of monthly streamflow, baseflow, or N-loads.

A field test on the use of anion exchange resin to remediate tile water for nitrate showed that nitrate adsorption by the resin is instantaneous. The efficiency of the resin to retain nitrate varied 7-46%. This efficiency generally decreased with time due to the presence of sulfate, bicarbonates, and organic anions in tile water, which competed with nitrate ions for adsorption to the resin. In some instances, nitrate concentration in the percolating water was higher than the tile water most likely due to the expulsion of adsorbed nitrate ions on the resin by sulfate ion in the tile water. The results also showed that potassium chloride (KCl) is an effective resin-regenerating agent and provides a means to recycle wastewater as KNO_3 fertilizer back on land.

Although the use of anion exchange resin is an attractive alternative to passive technologies like bioreactors, saturated buffers, control drainage, etc. for remediating nitrate in tile water, it also presents some challenges in its use under field conditions. These challenges include the fouling up of the resin by sediment, sulfate, bicarbonate, and organic anions in tile water; costs associated with buying of resin and regenerating salt (KCl versus NaCl); need for a large volume of clean water for cleaning of resin; and the difficulty of treating large volume of tile water in-situ. However, the feasibility study shows that small-scale units similar to home water softener can be developed for individual homes in rural area where groundwater may be high in NO_3-N concentration and NO_3-N remediation is needed.

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INTRODUCTION TO THE THESIS

The northern part of the Gulf of Mexico, where the Mississippi River enters, is the largest body of hypoxic water in the western Atlantic Ocean (Goolsby et al., 2001). This hypoxic zone has been ever-increasing since its monitoring began in the early-1970's (Rabalais et al., 2001) and even more so when mapping began in 1985 (NOAA, 2017). In August 2017, it was the largest hypoxic zone ever spanning a total of 22,730 square kilometers and extending from the inner- to mid-continental shelf at depths of 5 to 60 m (NOAA, 2017). Scientists believe the hypoxic zone in the Gulf of Mexico is caused by an increasing amount of nitrate discharged by the Mississippi River into the Gulf of Mexico. The presence of high levels of nitrate leads to increased algal productivity, which on decay leads to low dissolved oxygen (<2 mg L^{-1}) in the water near the bottom layers of the Gulf (Rabalais et al., 2001). Besides the excess nutrients drained into the Gulf via the Mississippi River, seasonal stratification of gulf waters is another reason for the hypoxic conditions.

Much of the nitrate in the Mississippi River is from agricultural lands in the Midwestern United States. Goolsby et al. (2001) suggested that the Dead Zone has been increasing over the past 200 years because of agricultural intensification in the Midwest. Every spring, N compounds in farm runoff enter the Mississippi River and contribute to the development of hypoxic zone in the Gulf. In May 2004, a total of 104,000 metric tons of nitrate washed into the Gulf (Tomer and Schilling, 2009). Goolsby et al. (2001) estimated that Midwestern agriculture (Minnesota, Iowa, Illinois, Indiana, and Ohio) contributes >3100 kg N km^{-2} to streams each year. Most of the nitrate losses from

Midwest agriculture are generally through tile drainage. Specifically, in the Upper Midwestern states, like Minnesota and Iowa, farmers have installed subsurface drain tiles that take excess water out of the field. The reason for installing drain tiles is the presence of impeding layers that restrict rainwater percolation causing the development of perched water table conditions. Kanwar et al. (1988) concluded that if farmers in the Upper Midwest do not drain their land, it will affect their crop productivity from limited rooting depth. Furthermore, tile drainage helps to reduce soil moisture such that field operations like tillage, planting, and harvest can be done in a timely manner.

More than any other nutrient, nitrogen (N) is taken up by crops in large quantities (Kladivko et al., 2004). As the plant size increases so does its need for N (Hobson and Page, 1932). To offset N deficiency in most soils, farmers apply N-fertilizer either in inorganic or organic form (manure). N-fertilizer addition not only increases crop yield but also its quality. However, a consequence of applying N-fertilizer (depending on the time of application and amount applied) is some loss of N from agricultural landscapes. Since nitrate is a negatively charged anion it does not bind strongly to the soil particles. As a result, nitrate is mobile in the soil and during wet conditions can travel to groundwater or leave the landscape through agricultural drain tiles. The N flux during wet years can increase by 50% or more if the previous years were dry and the soil-stored nitrate-N from these years was flushed out by subsequent year’s heavy rains.

For many years, the primary focus of nitrate leaving the root zone has been on nitrate entering the groundwater and thus contaminating the drinking water supply. The current drinking water standard is 10 mg L^{-1} NO_3-N. In the past, the presence of nitrate in surface waters has been overlooked, primarily because phosphorus is typically the limiting nutrient for algal productivity in surface waters. With the ever-increasing installation of drain tiles in agricultural landscapes of the Midwest and the resulting delivery of higher nitrate loads to the Gulf of Mexico, there is an increased focus on managing nitrogen inputs to land as well as finding ways to remediate nitrate in tile water. A literature review of drainage studies worldwide shows annual NO_3^--N loss via tile lines can vary from 0 to 138 kg ha^{-1} (Randall et al., 1997). These studies further show that even plots devoid of vegetation result in average annual loss of 22 kg NO_3-N ha^{-1} (Randall et al., 1997). The source of this nitrate loss is mainly from the mineralization of soil organic matter. In the same study, these authors found that corn and soybean grown without additional N fertilizer lost 11 kg ha^{-1} NO_3-N. At near-optimum N application rates, annual NO_3-N losses from row crops of corn in wet years ranged from 17 to 45 kg ha^{-1} (Randall et al., 1997).

Another six-year study at Waseca, MN showed that fall applications of N-fertilizer (urea) with or without a nitrification inhibitor had similar NO_3^- losses as spring application of N-fertilizer with or with a nitrification inhibitor (Randall and Vetsch, 2005). On average, NO_3-N losses over 6 years were 1.25, 1.12, 1.08, and 1.17 kg ha^{-1} cm^{-1} of tile water from fall-applied urea, fall-applied urea with nitrapyrin, spring applied urea and spring applied urea with nitrapyrin, respectively. However, these N losses varied from year to year depending upon the weather conditions. In general, over 70% of all N losses through drain tiles occur from April through June in the Upper Midwestern United States. The N losses from agricultural lands not only depend upon the available N in soils (from N-fertilizer application and mineralization) but also on the availability of percolating water from precipitation. Recent National Climate Assessment shows that precipitation has been increasing in the Midwest (USGCRP, 2017). For example, there has been an increase of 10% to >15% in precipitation from 1991-2011 relative to 1901-1960 in the upper Midwest (Melillo et al., 2014). At some locations in the upper Midwest, such as Waseca, MN, annual precipitation has increased by as much as 200 mm yr^{-1} in recent years (1978-2007) compared to 1921-1950 (Mark Seeley, University of Minnesota, personal communication, 2013). Recent research also shows that precipitation not only from the current year but also from the previous year influences streamflow and baseflow in the Upper Midwest (Gupta et al., 2017). Thus, the question arises: How are changes in climate (increased precipitation) impacting annual and monthly NO_3^- loads and the flow-weighted N concentration in watersheds of the Upper Midwest? As there has been a continued adoption of soybeans replacing small grains since the 1940's, another question to explore is: How is increasing soybean area in agricultural landscape affecting river water quality in terms of NO_3-N losses?

Use of sustainable farming techniques and planting of crops that have a higher potential for nitrate uptake can reduce the amount of nutrients entering the Mississippi River. Another way to reduce NO_3-N losses from agricultural lands to rivers is through use of remediation technologies including passing tile water through wetlands (Christianson et al., 2016). Some of these remediation technologies include woodchip bioreactors, saturated buffer strips, controlled drainage, and cover crops. However, many of these technologies require higher residence time for drainage water to remediate. As a result of this limitation, these technologies have met a varied degree of success. In urban areas where nitrate levels are often high in source water for drinking, nitrate polluted water is generally passed through industrial resin similar to a water softener and stripped of its NO_3^- contents. The main advantage of using industrial resin is the instantaneous removal of NO_3^- as well as reusability of the resin, thus being cost effective in the end.

The objectives of this thesis research were (1) to evaluate the impact of changing climate (increased precipitation) and land use (tile drainage and adoption of soybeans) on streamflow, baseflow, NO_3–N concentrations and NO_3-N loads in the Des Moines River, the Iowa River, and the Raccoon River in Iowa, and (2) to evaluate the feasibility of using industrial anion resin to remediate nitrate from tile water at the edge of agricultural fields. The premise of the first objective is an improved understanding of factors affecting increased NO_3-N loads in rivers of the Upper Midwest and in turn on the increasing hypoxic zone in the Gulf of Mexico. The second objective evaluates the potential of using anion resin to remove NO_3^- from tile water in agricultural settings as well as to evaluate if potash (KCl) instead of common salt (NaCl) can be used for regenerating anion resin such that the waste (KNO_3) can be recycled back to land as a fertilizer.

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CLIMATE AND LAND USE CHANGE IMPACTS ON NITROGEN LOADS IN THREE IOWA RIVERS

SYNOPSIS

The Upper Midwest United States has undergone scrutiny for excess nitrogen (N) entering the Mississippi River via agricultural drainage and then contributing to the development of hypoxic zone in the Gulf of Mexico. Iowa, in particular, is a major producer of agricultural crops and has numerous rivers that carry high N-loads to the Mississippi. This study evaluated how increased precipitation and land use land cover changes might be impacting N-loads in three major Iowa Rivers; the Des Moines River, the Iowa River, and the Raccoon River. This evaluation was done using the backward stepwise regression analysis on annual and monthly streamflow, baseflow, flow-weighted N concentration, and N-loads with annual or monthly precipitation and annual soybean area as a surrogate for land use land cover changes. Results showed that both streamflow and baseflow were impacted by the current year and by the previous year precipitation. Annual scale Ln(N loads) were primarily controlled by the precipitation in the corresponding watershed. Since river N-loads are a product of N concentration and streamflow, the exponential increase in N-loads with precipitation was due to an exponential increase in streamflow and baseflow with precipitation. For the Raccoon River, N loads were controlled by the current year and previous year precipitations comparatively, for the Des Moines and the Iowa Rivers, N loads were only related to the current year precipitation. Presence of previous year precipitation in streamflow,

baseflow, and N loads regressions reflected the lack or excess presence of stored water in the soil and its consequences on overland flow, infiltration, and percolation processes. Effect of land use change in terms of increased soybean area (comparatively decreased areas undersmall grains), had no effect on Ln(annual streamflow), Ln(annual baseflow), annual flow-weighted N concentrations or Ln(annual N-loads) in all three rivers.

Statistical analysis of the combined annual data from all three rivers showed that the relationship between the streamflow, the baseflow, and the N-yield (N loads/watershed area) with precipitation were nearly similar for all three rivers. Furthermore, the precipitation effects were present both in terms of the current year and the previous year precipitation. The coefficient of determination (R^2) of Ln(streamflow), Ln(baseflow) and Ln(N yield) for the combined data were 0.74, 0.70 and 0.54, respectively. Limited scatter in the N-yield data at a given annual precipitation over three rivers suggested that differences in cultural or cropping practices among the three watersheds likely had a minimal impact on N yield. Comparatively, inter-annual variability in precipitation varying from 500 mm to over 1200 mm has a much bigger impact on variation in N yields within a given watershed as well as between the watersheds. Considering that there has been a 10-15% increase in precipitation in the Upper Midwestern United States in recent years, the combined N-yield relationship with precipitation would suggest that the recent increases in N-loads or increased hypoxic area in the Gulf of Mexico are likely due to recent increases in precipitation.

Regression analysis of monthly streamflow, baseflow, N-loads and FWNC concentration showed that LN(streamflow), Ln(baseflow), and Ln(N-loads) were generally related to precipitation in a given month and a few prior months. In some cases earlier in the season, the above predictor variables were also related to previous year's precipitation, an indication that some of the past water stored in the soil both above and below the drain tile is interacting with current month's precipitation and affecting the streamflow and baseflow. In most cases, there was no effect of soybean area on monthly streamflow, baseflow, or N-loads.

INTRODUCTION

Agricultural practices in the Upper Midwest have been linked to the presence of excess nitrogen (N) in many rivers of the Mississippi River valley and this, in turn, has led to the development of hypoxic zone in the Gulf of Mexico. Development of hypoxic conditions (oxygen levels <2 mg/L) affects the fisheries especially the shellfish and in turn the livelihood of many residents in that area. According to EPA, the hypoxic zone has varied from less than 500 km^2 in 1988 to over 22,730 km^2 in 2017 (https://www.epa.gov/ms-htf/northern-gulf-mexico-hypoxic-zone). Long-term (1985-2014) average mid-summer hypoxic zone in the Gulf of Mexico is around 14,000 km^2. In recent five years (2010-2014), this hypoxic zone has averaged around 15,000 km^2.

Two major practices blamed for discharge of excess N to rivers are (1) the installation of subsurface drain tiles in agricultural fields (Kenney and DeLuca, 1993; Goolsby et al., 1999; Randall et al. 2008; Ikenberry et al., 2014) and (2) the use of nitrogenous fertilizers and manure in agricultural production (Alexander and Smith, 1990; Lucey and Goolsby, 1993; Rabalais et al., 1998; Goolsby et al., 1999 and 2001; and Petrolia et al., 2006). Although there are no good records of the length of drain tile installed in the Upper Midwest, there is a good consensus that the area brought under agricultural drainage has been steadily increasing since the mid-1970's right after the plastic drain tile started being manufactured (1967) in the United States (Gupta et al., 2015). Hatfield et al. (2008) showed that the land use practices, specifically the increased installation of drain tiles, has dramatically increased the amount of N and phosphorus loss from the Raccoon River watershed. Since nitrate (NO_3) and nitrite (NO_2) are readily soluble in water, anytime water goes through the soil to the drain tile, it carries with it soluble salts, including NO_3 and NO_2. Goolsby et al. (2001) estimated a mean annual NO_3-N flux of 0.95 million metric tons from the Mississippi-Atchafalaya River Basin to the Gulf of Mexico from 1980-1996. Total N flux (nitrate-N, ammonium-N, dissolved organic N and particulate organic N) contributions from the above basin corresponded to 1.57 million metric tons. These authors concluded that the principal source areas of N were watersheds in Southern Minnesota, Iowa, Illinois, Indiana, and Ohio. Nitrate-N concentration for the Raccoon River (6.67 mg L^{-1}) and the Des Moines River (4.12 mg L^{-1}) in Iowa were among the highest in the Mississippi River Basin (Goolsby et al., 2001). David et al. (2010) showed that it is not uncommon to find NO_3-N concentrations of 20 to 50 mg L^{-1} in tile-drained waters from agricultural fields in Illinois. However, Ikenberry et al. (2014) showed that NO_3-N concentrations are generally higher from plot studies than those found in small watersheds even though water yields are similar. For example, five-year (2009-2013) average NO_3-N concentration for the Boone River and its three catchments in Iowa were 11 mg L^{-1} versus 29 mg L^{-1}, respectively. However, the corresponding five-year average water yield was similar (253 mm and 248 mm, respectively). This difference in concentration resulted in a NO_3-N yield of 27.2 kg ha^{-1} yr^{-1} for the Boone River versus 39.8 kg ha^{-1} yr^{-1} for its three catchments.

Iowa waterways have especially shown increasing NO_3-N concentrations in recent years. The United States' regulated concentration of NO_3-N in drinking water is

10 mg L^{-1}. For the period 1974 to 1990, NO_3-N concentration in the Raccoon River exceeded the drinking water standard for 170 days and 137 days in June and May, respectively (Lucey and Goolsby, 1993). The smallest numbers of days exceeding the standard of 10 mg L^{-1} during the above period were three days in September. In 1990, NO_3-N concentrations at public water-supply intakes on the Des Moines and the Raccoon River in Iowa exceeded the 10 mg L^{-1} limit from March to early August. On an annual basis, 1980 and 1979 had the highest number of days (106 and 95, respectively) exceeding the drinking water standard in the Raccoon River (Lucey and Goolsby, 1993).

Twenty percent of Iowa's population relies on surface water for their supply of drinking water (USGS National water summary 1990-91). For decades there has been a growing concern on the use of high NO_3 containing water from Iowa's rivers for drinking water supply. In 2015, Des Moines Water Works sued three Iowa counties, Sac, Calhoun, and Buena Vista, for high levels of NO_3-N in their drainage ditches contributing to the Raccoon River and in turn threatening the lives of 500,000 central Iowans. The suit claimed that discharging high NO_3 concentrations into the Raccoon River was without a federal permit, which according to Des Moines Water Works, was violating the Clean Water Act. However, the Clean Water Act has always exempted runoff from farms and irrigation because it is not a point source (subsurface tile drainage is categorized as groundwater). Des Moines Water Works argued that it should be considered as point source pollution, especially when they are spending $7,000 a day to remove NO_3 that is discharged upstream. In March of 2017, the lawsuit was dismissed, saying that Iowa water quality is a matter for the legislature to solve. However, the fight added energy to the growing debate about Iowa's water quality, primarily, who is responsible and what can be done to solve it (https://www.calt.iastate.edu/article/des-moines-water-works-litigation-resources).

In addition to studies linking tile drainage and fertilizer use on NO_3 levels in Iowa and other Midwestern rivers, recent studies have also linked changes in land use and land cover (LULC) practices such as adoption of soybeans to increased streamflow as well as to poor water quality. For example, Schilling et al. (2005) and Jones et al. (2016) have suggested that increased soybean area is one of the main reasons for high NO_3 loads in Iowa's rivers. These authors reasoned that since soybeans are planted later in the season compared to small grains prior to the 1940's, this resulted in less ET in early spring and thus, higher baseflow and more N loss (Schilling and Libra, 2000; Schilling and Zhang, 2004; Schilling and Lutz, 2004; Schilling, 2005). Jones et al. (2016) further implied that since soybean residue mineralization rates are 1.5 times greater than non-legume crops, soybean addition in the cropping system may be contributing additional N inputs and increasing N losses through tile drainage. However, many of these studies have ignored or minimized the impact of changing climate on increased flows and N-loads in Iowa's rivers. For example, Zhang and Schilling (2006) assumed that there is minimal to no change in precipitation between the pre-LULC change (prior to 1940) and post-LULC change (after 1940) periods and thus, increased streamflow (51%) and baseflow (66%) are mainly due to changes in LULC especially the adoption of soybeans in the cropping system. However, it is well established that there has been at least 10-15% increase in annual precipitation in Iowa from 1991-2012 relative to 1901-1960 (Melillo et al., 2014). In some areas, the increase was 5-10% and in others, it was >15%. Figure 1 illustrates the increasing amount of precipitation that Iowa has experienced from 1920-2009 (Gupta et al., 2015). The figure is separated into three time periods, 1920-1949, 1950-1979, and 1980-2009. Considering trends in increased precipitation in Iowa (Figure 1), it is not surprising that drain tile installation has increased since the 1970's (to accommodate an average of 850 mm rainfall). In addition to increased precipitation, there has also been a 37% increase in the amount of precipitation in very heavy events (the heaviest 1% of all daily events) from 1958 to 2012 (Melillo et al., 2014). The National Climate Assessment also shows that besides increased precipitation, there has also been 0.5-1.0 °F increase in average air temperature in Iowa from 1991-2012 compared to 1901-1960 (Melillo et al., 2014). In some Iowa locations, the increase was between 1.0 to 1.5 °F. Pryor et al. (2013) have shown that since the 1950's the growing season of the Midwest has expanded by two weeks due to increased temperatures, an effect that will only continue to grow (estimated to be a three-week increase by 2041-2062). Although the increased growing season could potentially improve crop yield, it also could lead to an increase in soil mineralization and thus higher N-loads in various river systems. Then the question is: How have increased precipitation, warmer temperatures, and changed cropping systems (increased area under soybean) impacted streamflow, baseflow, flow weighted N- concentration and N-loads in various rivers of the Upper Midwest especially in Iowa?

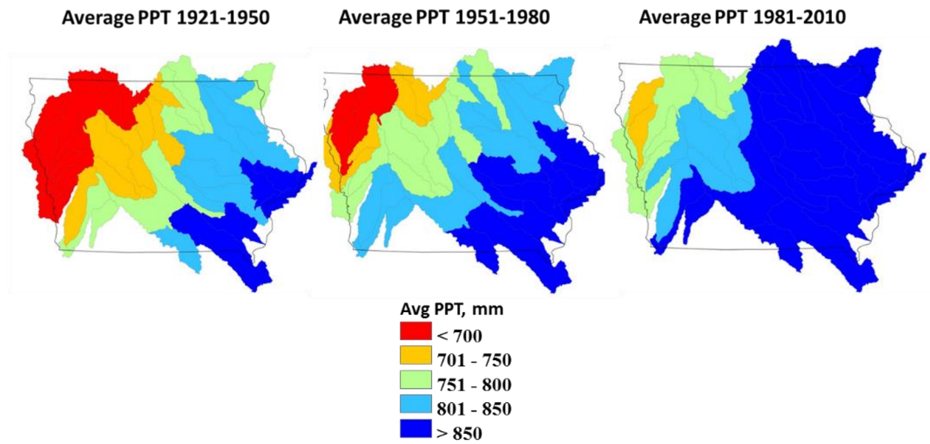


Figure 1: A comparison of Iowa 30 year normal precipitation from 1921-1950, 1951-1980, and 1981-2010.

There is limited literature on climate impacts on various NO_3-N-loads in rivers of the Upper Midwest. In fact, some investigators have often assumed no change in climate (Kenney and DeLuca, 1993; Zhang and Schilling, 2006). For example, Keeney and DeLuca (1993) showed that annual and weekly NO_3-N concentrations in the Des Moines River were positively related to corresponding streamflow values from 1980-1990 but the average NO_3-N concentration and streamflow over 11 year period were similar to the corresponding values in 1945. These authors, thus, inferred that factors other than N fertilizer use must be the cause of high NO_3-N contamination in surface waters of Iowa. However, these authors ignored the changes in climate (increased precipitation and temperature) and suggested changes in land management, cropping patterns, and land use changes (especially enhanced mineralization of soil N coupled with subsurface tile drainage) as possible factors. In a subsequent analysis, McIsaac and Libra (2003) showed that 1945 arithmetic average NO_3-N concentration used by Kenney and DeLuca (1993) was between 44-57% of the 1976-2001 expected value due to uncertainty associated with averaging technique and sampling locations. Now the question is: are some of the differences in NO_3-N concentration between 1976-2001 vs. 1945 in Des Moines River due to N fertilizer use, climate change, or both?

Lucey and Goolsby (1993) indirectly commented on the role of climate on increased N-loads in the Des Moines and the Raccoon Rivers in Iowa. They noted that higher N-loads followed two less than normal precipitation years (1988, 1989) in 17 years of history and thus suggested that during precipitation deficient years, NO_3-N must be accumulating in the soil both due to less transport as well as due to decreased plant uptake. In other words, it is the accumulated NO_3-N that got mobilized in 1990, an above average precipitation year. These authors suggested a four-variable model that explained 70% of the variability in NO_3-N concentrations of the Raccoon River. Among the four variables, mean streamflow for the previous seven days explained 50% of the variability. The other important variables were the soil-moisture conditions and sine and cosine function of time. In the Embarrass and the Kaskaskia Rivers of Illinois, Gentry et al. (2014) showed that the current water yield accounted for 87% and 79% of the variability in annual NO_3-N yield. Further addition of previous year's water and corn yields, as well as the amount of fall-applied N fertilizer in the regression, explained a total of 96% of the variability in annual NO_3-N yield in these rivers. Regression coefficients for previous year's water and corn yield were negative which means low water yield in the previous year indicates there is stored NO_3^- in the soil that will be available for leaching in the current year. Conversely high water yield in the previous year indicates less NO_3-N is available for leaching in the current year. Similar to water yield, low corn yield in the previous year means more available NO_3 in the soil for current year leaching. Since water yield from a watershed is related to precipitation, this shows that there must be some relationship between NO_3-N in rivers and precipitation in the area.

Recently, Gupta et al. (2015, 2016a) showed that both annual streamflow and baseflow of rivers in the Iowa and Minnesota are exponentially related to precipitation not only in that year but also with precipitation in the previous year(s). Prior year(s) precipitation accounted for water storage (affecting the quantity of discharge) and surface soil wetness differences (affecting the runoff and infiltration processes). A subsequent analysis further showed that monthly discharge was also related to a given month's and previous months' precipitation as well as previous years' precipitation (Gupta et al., 2017). This raises the question: is there any relationship between annual and monthly NO_3-N-loads and flow-weighted N concentrations (FWNC) to corresponding annual and monthly precipitations and temperatures? Furthermore, what is the role of increasing soybean area (or conversely decreasing small grains area) in affecting river water quality in terms of NO_3-N-loads and FWNC? The goal of this study was to assess climate and land use land cover (LULC) change effects on stteamflow, baseflow, flow weighted N concentrations, and N-loads in three of Iowa's rivers: The Des Moines River, the Iowa River, and the Raccoon River.

METHODS

Study Area

As a consequence of four periods of glaciation (Nebraskan, Kansasan, Illinoian, and Wisconsinan), Iowa became a landscape rich with fertile soils and a variety of rivers. The topsoil of Iowa has been dubbed as “black gold” primarily because the soils in the area are black in color (high in organic matter) and produce high crop yields. The source of high organic matter in Iowa’s soils is the result of an extensive network of prairies that once covered this landscape. Prairies having fibrous roots and substantial aboveground biomass, both of which decomposed over time and contributed to high organic matter and thus to the black color of the soil.

This paper focusses on three Iowa’s rivers: The Des Moines River at the 2nd Avenue Bridge (USGS Gage # 05482000; Fig. 2a), the Iowa River at Wapello (USGS Gage # 05465500; Fig. 2b), and the Raccoon River at Van Meter (USGS Gage # 05484500; Fig. 2c). Watershed characteristics of the three rivers are given in Table 1. Annual and monthly streamflow and nitrogen (NO_3+NO_2) data for Des Moines and Iowa rivers were taken from the United States Geological Survey open file report (Aulenbach et al., 2007) (https://toxics.usgs.gov/hypoxia/mississippi/flux_ests/all/index.html), annual and monthly precipitation data for all three watersheds were downloaded from the PRISM Climate Group website (http://www.prism.oregonstate.edu/), annual Iowa fertilizer use data was acquired from the USGS’s National Water-Quality Assessment Program county level estimates (Ruddy et al., 2006; https://pubs.usgs.gov/sir/2006/5012/), and the statistics on crop area for these watersheds were downloaded from the National Agricultural Statistics Service (NASS) database (http://quickstats.nass.usda.gov). Monthly and annual N loads were divided by the corresponding flow to calculate the monthly and annual FWNC. Streamflow and daily nitrogen loads and concentrations for the Raccoon River were acquired from the Des Moines Water Works (Personal Communication, Jeff Mitchell, 2015). The daily flow was the sum of the daily flows in the Raccoon River as well as in the Walnut Creek. Monthly and annual baseflows for all three watersheds were calculated from the daily streamflow data using the USGS PART program (Rutledge, 1998). Since we used the daily flow from Van Meter gauge site for the Raccoon River baseflow calculations, it does not include the baseflow contributions from the Walnut Creek. However, considering the Walnut Creek streamflow is about 5% of the Raccoon River flow at Van Meter, its contributions to baseflow will be relatively small.

Table 1: Drainage area, average precipitation, and percent area under corn-soybean cropping system in watersheds contributing N load to the Des Moines, Iowa, and Raccoon Rivers in Iowa.

Watershed	Years of data used	Gage ID	Gage location	Drainage area (km^2)	Precipitation † (mm)	% Area Corn-Soybean†
Des Moines River	1984-2014	05482000	2nd Ave Bridge	16,174	916	78%
Iowa River	1978-2013	05465500	Wapello	32,375	845	74%
Raccoon River	1974-2011	05484500	Van Meter	8,912	824	76%

†Average over 30 years, 1981-2010

The Des Moines River

The Des Moines River is 845 km long and is the longest river in Iowa. Its headwaters begin at Lake Shetak in Minnesota and from there it runs down to central Iowa and joins the Mississippi River near Keokuk. The Des Moines River is located in the Des Moines Lobe region of Iowa which has poor surface drainage due to low relief. Total drainage area of the Des Moines River at 2nd Ave Bridge in Des Moines is 16,174 km^2; 78% of which is under row crops of corn and soybeans; 18.5% is forest, grasslands, and wetlands; and 2.5% is under urban use (Schilling and Wolter, 2009). Average annual precipitation from 1995 to 2006 varied from 785 mm at Algona to 810 mm at Ft. Dodge; two major cities in the Upper Des Moines River (Schilling and Wolter, 2009). From 1982 to 2013 the average annual discharge was 8,678 $m^3\ s^{-1}$. Soils in the Des Moines River Watershed are developed from glacial till parent material and are primarily clay loam in texture.

The Iowa River

The Iowa River is 480 km long and is a primary tributary to the Mississippi River. The Cedar River is the major tributary of the Iowa River which begins partially in southeastern Minnesota and joins the Iowa River in Louisa County. There are two headwater sources for the river, the East and the West branches, both beginning in Hancock County, IA and joining together in Belmond, IA. Total drainage area of the Iowa River watershed at Wapello, IA is 32,375 km^2 out of which 74.2% is corn and soybean, 9.3% is residential, 6.2% is hay, 5.7% is grass or prairie, 3.3% is forest, and 1.3% is other (from the National Land Cover Data; NLCD, 2001). From 1965-2014, the annual average precipitation in the watershed was 907 mm/yr and the annual average discharge from 1968-2014 was 432 $m^3 s^{-1}$. The soils in the watershed are partially developed from loess and partially from glacial till parent materials (NRCS, 2011).

The Raccoon River

The Raccoon River is 364 km long and is located in central Iowa. The Raccoon River is a tributary of the Des Moines River and thus also a contributing river to the Mississippi River. The Raccoon is separated into three sections: the North Raccoon (315 km), the Middle Raccoon (148 km), and the South Raccoon (116 km). The North and South Raccoon meet just west of Van Meter, IA; location of USGS gage. It eventually joins the Des Moines River in the city of Des Moines. The drainage areas of the Raccoon river is approximately 8,912 km^2, of which 76% is under row crops of corn and soybean, 17% is grassland, 4% is forest, 2% is urban use, and 1% is water (Schilling et al., 2008). Due to heavy agricultural land use in the Raccoon River watershed, the river water quality has been a growing concern especially in terms of nitrate and nitrite entering the surface waters. According to Schilling et al. (2008), row crop area in the basin increased by 36% from 1940 to 2005 with much of the increase coming from area that was previously under small grain and some from new lands that were under natural vegetation.

A major use of the Raccoon River is as a water supply for the city of Des Moines since the 19^{th} century. Nitrate concentrations in the river have frequently spiked above the regulated drinking standards. The soils in the watershed are primarily developed from the glacial till parent material and are poorly drained. The landscape in both the north and middle Raccoon Rivers has relatively low relief (2 to 5%, Schilling et al., 2008). Forty-nine percent of agricultural land in the Raccoon River watershed is estimated to have subsurface drainage (Raccoon River Watershed Water Quality Master Plan). Schilling and Wolter (2007) estimated that 77.5% of the North Raccoon portion of the watershed was tile drained compared to 42.1% in the South Raccoon. From 1981-2010, the annual average precipitation in the watershed was 824 mm yr^{-1} whereas the annual average discharge from 1965-2014 was 272 $m^3\ s^{-1}$.

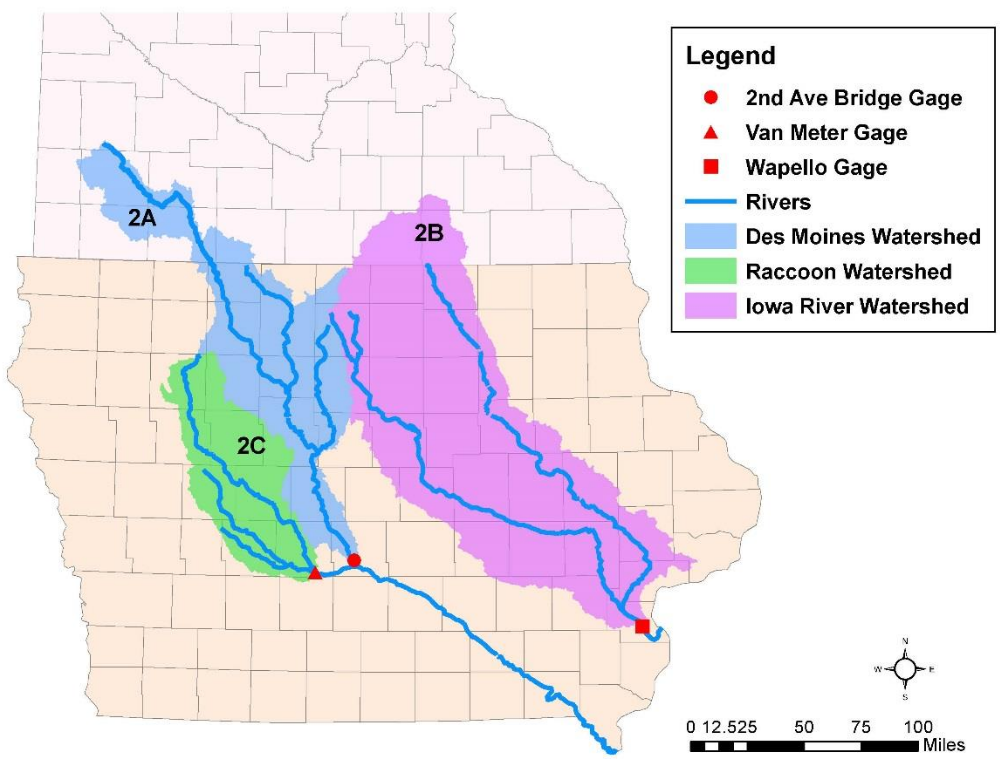


Figure 2a-c: A map outlining watershed areas of the Des Moines River above 2nd Ave. Bridge (Fig. 2a), the Iowa River above Wapello (Fig. 2b) and the Raccoon River at Van Meter (Fig. 2c).

Data Analysis

The procedure for assessment of climate and LULC change effects on streamflow, baseflow, N-loads and FWNC in each river was similar to the approach used by Gupta et al. (2015 and 2017). Briefly, the procedure involved a backward stepwise multiple regression of Ln(streamflow), Ln(baseflow), Ln(N loads), and NO_3+NO_2 flow-weighted concentrations (FWNC) as the predictor variable and precipitation, air temperature, and soybean area as the explanatory variables. Before regression, predictor variables were tested for normal distribution using the Shapiro-Wilk test and in most cases, a natural logarithmic transformation was needed to transform the data to a normal distribution; a finding similar to that of Schilling and Libra (2003). In the case of annual data analysis, the explanatory variables included not only the precipitation in a given year (P_1) but also in previous 2-3 years (P_2, P_3). Since previous studies in Iowa had suggested LULC change (adoption of soybeans in lands that were previously in small grains and under natural vegetation) as an important variable, we included present year soybean area (SB_1) as well as soybean area in the previous year (SB_2) as explanatory variables in the regression (Eq. 1).

$$\ln(Predictor\ Variable) = \beta_0 + \beta_1\ X\ P_1 + \beta_2\ X\ P_2 + \beta_3\ X\ P_3 + \beta_6 XSB_1 + \beta_7 XSB_2 + \beta_8 XT + e$$

(Eq. 1)

where predictor variable can be the annual streamflow, annual baseflow, annual N-load, or annual FWNC; β_0 to β_8 are the regression coefficients; P_1, P_2 …P_3 are precipitation in a given year to 2 prior years; SB_1 and SB_2 are soybean area under current and previous year; T is the average annual air temperature of a climatic division most representative of the watershed.

In the case of monthly data analysis, the predictor variables were Ln(monthly streamflow), Ln(monthly baseflow), monthly (N-loads), or FWNC and the explanatory variables were the monthly precipitation for the current month and all previous months to January, previous year precipitation and the previous year soybean area (Eq. 2). Backward stepwise regression involved stepwise deletion of explanatory variables from the regression that did not meet the significant criteria of α = 0.05. The probability of a given variable in the regression was taken from analysis of variance (ANOVA) tables generated during regression. Durbin-Watson statistics was also run on residuals to ensure that there was no autocorrelation between explanatory variables in the regression.

$$\ln(Predictor\ Variable_{Given\ Month}) = \beta_0 + \beta_1\ X\ P_{Prev\ Year} + \beta_2\ X\ Sb + \beta_3\ X\ Sb_{Prev\ Year} + \beta_4\ X\ P_M + \beta_5\ X\ P_{M-1} + \beta_6\ X\ P_{M-2} + \cdots + \beta_{M-N} X P_{M-N} \quad \textit{(Eq. 2)}$$

where Predictor $\text{Variable}_{\text{Given Month}}$ can be a given month's streamflow, baseflow, N-load, or flow-weighted N concentrations; $P_{\text{Prev Year}}$ is the precipitation in the previous year; Sb is the area under soybean in the given year; $Sb_{\text{Prev Year}}$ is the area under soybean in the previous year; P_M is the precipitation in the given month; P_{M-1} is the precipitation in the month before; and P_{M-N} is the precipitation in the N^{th} previous month. Depending on the given month, N could vary from 2 (February) to 11 (November). In other words, regression analysis for streamflow in March will have M=3 and N=2 (January and February). Similarly, regression analysis for the month of December (M=12) will have N=11 (January to November). This analysis was done using the Excel data analysis tool (Microsoft Office, 2009). The flow-weighted N concentrations in most cases did not require a natural logarithmic transformation to make the data a normal distribution. Thus, the regression analysis for flow-weighted N concentration was run without any transformations. Annual precipitation, streamflow, baseflow, N-loads, and N concentrations data were also tested for temporal trends using the Mann-Kendall test. These trend analyses and estimation of the Sen's slope were done using XLStat (2015). The Mann-Kendall trend test is a nonparametric test and is particularly useful when there are missing values and the data do not conform to a given distribution (Gilbert, 1987). It is different than the regression relationship where the test of data normality is a pre-requisite. It is commonly used in trend analysis of environmental, climate, or hydrological data series. A null hypothesis (H_0) indicates there is no trend in the series, alternatively, the series could result in the following trends: negative, non-null, or positive. Briefly, the test involves calculating the number of times the values increase over time minus the number of times the values decrease over time in the data set. A positive difference indicates increasing trends whereas a negative difference indicates a decreasing trend. The Sen's slope is an extension of the Mann-Kendall procedure

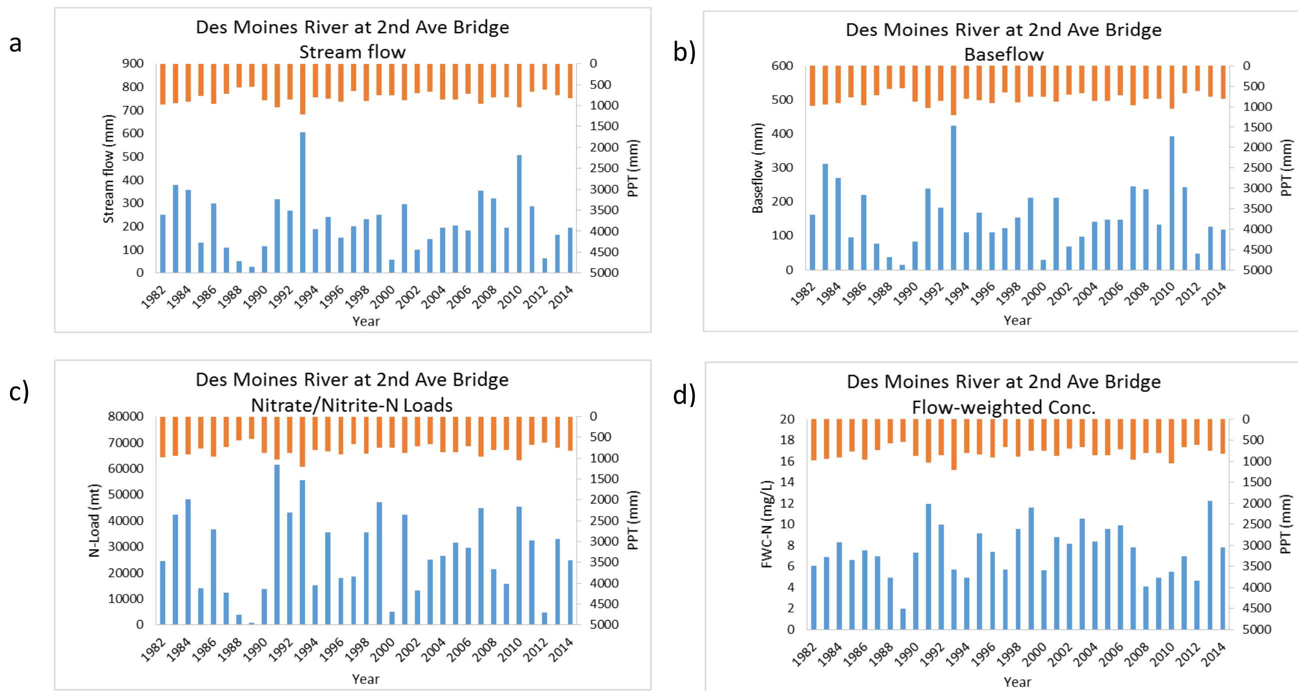
(Gilbert, 1987) and is also not affected by missing data or outliers. Basically, Sen's slope represents the median slope of all the sequential data (Gilbert, 1987).

RESULTS

The Des Moines River

Annual Analysis

Temporal distribution of annual streamflow (SF), baseflow (BF), NO_3-N-loads, NO_3-N flow-weighted concentrations (FWNC) along with the annual precipitation for the Des Moines River are plotted in Fig. 3. The baseflow Index (BFI) for the Des Moines River over the study period corresponded to 72%. The probability of Mann-Kendall trend analysis as well as the Sen's slope of these trends are given in Table 2. The Mann-Kendall analyses indicate that none of the above parameters displayed any significant temporal trends over the study period. However, the temporal distribution graphs do show that streamflow, baseflow, and NO_3-N-loads were higher in 1993 and 2010 because there was more precipitation in those years. Streamflow graph (Fig. 3a) also shows that high flows in 1993 were not only due to more precipitation in that year but also from precipitation in previous two years (1991, 1992 being relatively wet years). One can also observe a similar phenomenon in Fig. 3 recognizing that for a similar amount of annual precipitation, the streamflow (Fig. 3a), baseflow (Fig. 3b), and NO_3-N-load (Fig. 3c) were not the same over the study period. This is partially because no two years have the same distribution of precipitation, the stage of crop growth when rainfall occurs, and their interactions. Furthermore, some of the precipitation from previous years remains in the soil and interacts with next year's precipitation thus affecting streamflow. Gupta et al. (2017) have shown that if the previous year was a dry year then streamflow will be less in the following year because of additional fillable porosity. In other words, streamflow, baseflow, and NO_3-N-loads will be affected by not only the precipitation in a given year but also by the precipitation in previous years. Plots of FWNC and precipitation with time did not show any consistent effect of precipitation on FWNC (Fig. 3d).



Figures 3a-d: Temporal distribution of annual streamflow (Fig. 3a), annual baseflow (Fig. 3b), annual N loads (Fig. 3c), and annual flow-weighted NO_3+NO_2 concentrations (FWNC) (Fig. 3d) for the Des Moines River at 2nd Ave. Bridge and the corresponding precipitation over the watershed.

Table 2: Sen's slope and the p-values of the Mann-Kendall temporal trend in annual precipitation, streamflow, baseflow, N loads, and FWNC in the Des Moines River at 2nd Ave. Bridge. Trend tests were run using the XLSTAT package.

Precipitation		Streamflow		Baseflow		N-Load		FWC-N	
p-value†	Sen's Slope	p-value	Sen's Slope	p-value	Sen's Slope	p-value	Sen's Slope	p-value	Sen's Slope
0.22	-3.80	0.99	0.05	0.88	0.46	1.00	1.37	0.76	0.013

†P value >0.05 indicates a non-significant temporal trend in the variable under consideration

As demonstrated by Gupta et al. (2015), flow in the river is primarily controlled by precipitation, especially in rainfed areas like central Iowa. Furthermore, the river flows exponentially increase with an increase in precipitation. This is primarily because the overland flow and infiltration processes in the landscape control the river flow and they are primarily exponential or power functions processes. For example, if the soil is dry, all the water is retained in the soil and there is no overland flow. On the other hand, when the soil is saturated, every mm of additional rain is lost as a mm of overland flow. A similar argument applies to infiltration processes; in dry soils infiltration rate is high and then it starts decreasing until it reaches a steady-state condition corresponding to soil's saturated hydraulic conductivity when the soil is saturated. These processes are well described by overland flow equations like the runoff curve method or the infiltration equations like those of Horton and Kostiakov's (Ravi et al., 1998).

Figures 4 to 7 show the relationship between annual streamflow, baseflow, NO_3-N-loads, and FWNC versus annual precipitation. Except for FWNC, the other three variables display an exponential function behavior. This is consistent with the overland flow and infiltration processes as well as with the statistical necessity that a natural logarithmic transformation of these variables is needed to transform them into normal distributions. NO_3-N-loads are also exponential because it is a derived variable calculated from instantaneous NO_3-N concentration and a streamflow value. Even though the FWNC follows a second-degree polynomial relationship with precipitation, it is a weak second-degree relationship with R^2=0.19 (Fig. 7). Since FWNC are in the narrow range of 4-10 mg/L, the exponential increase of N-load with precipitation suggests that streamflow is a more dominating variable than the NO_3-N concentration in N-load calculations. In other words, more precipitation will lead to exponentially more streamflow and baseflow and in turn exponential increase in NO_3-N-loads.

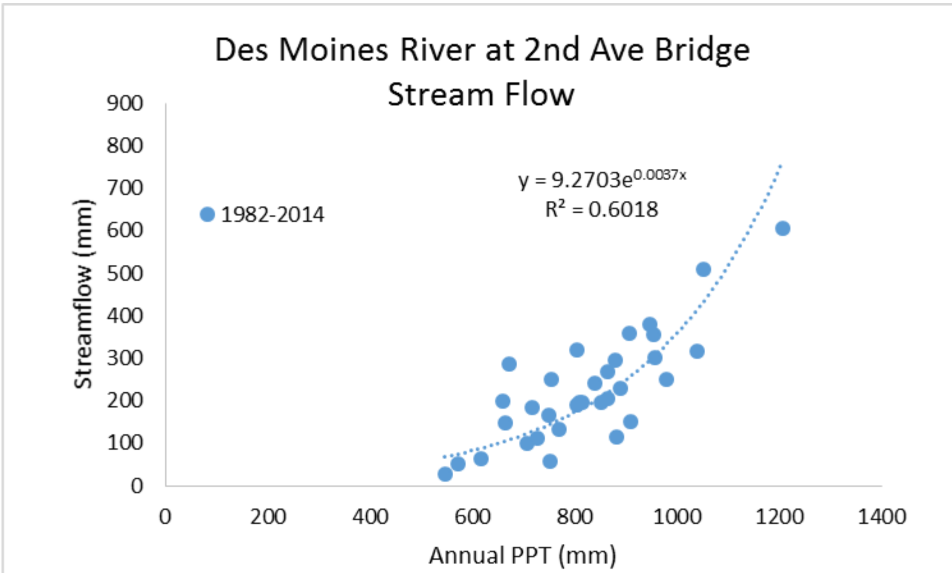


Figure 4: Relationship between annual streamflow for the Des Moines River at 2nd Ave. Bridge and the annual precipitation over the Des Moines River watershed

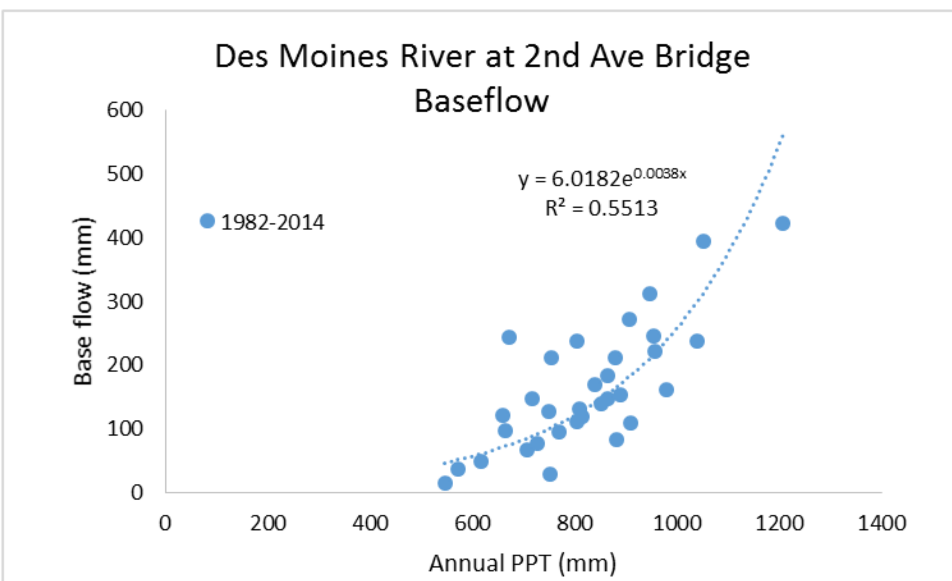


Figure 5: Relationship between annual baseflow for the Des Moines River at 2nd Ave. Bridge and the annual precipitation over the Des Moines River watershed

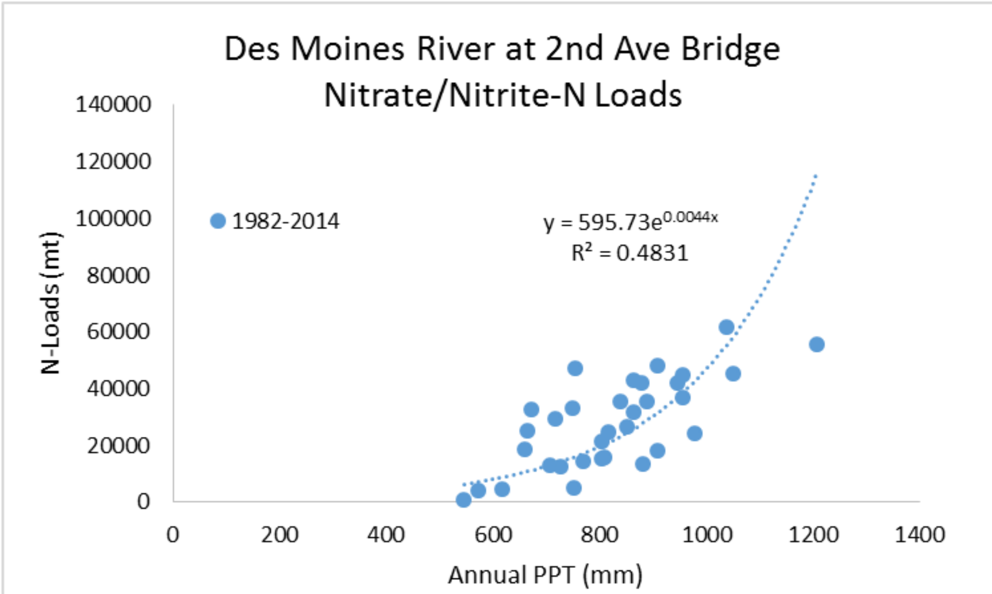


Figure 6: Relationship between annual NO_3-N loads for the Des Moines River at 2nd Ave. Bridge and the annual precipitation over the Des Moines River watershed

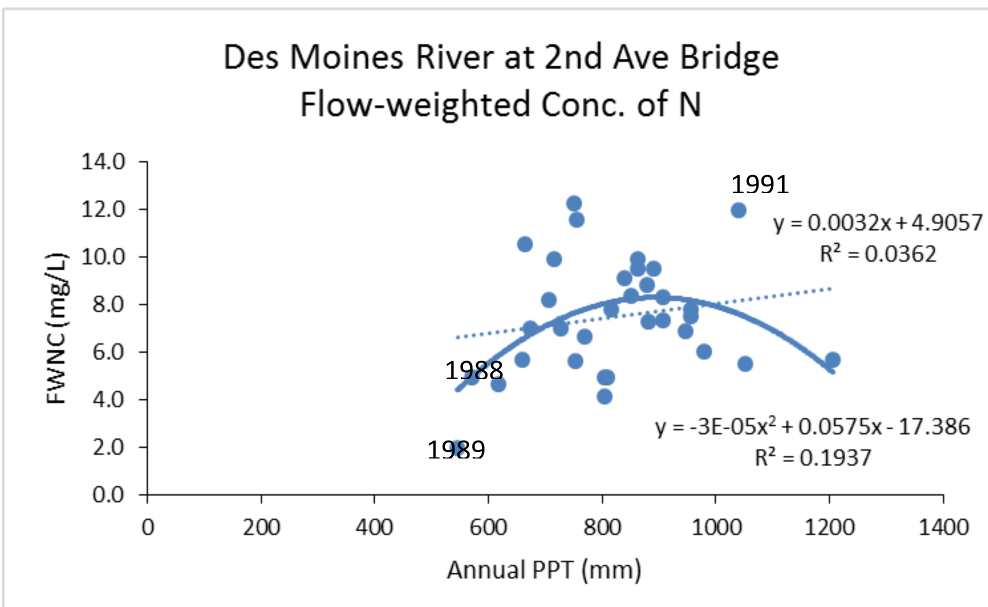


Figure 7: Relationship between annual flow-weighted NO_3-N concentrations (FWNC) for the Des Moines River at 2nd Ave. Bridge and the annual precipitation over the Des Moines River watershed

The p-values of current and previous year's precipitation along with area under soybean in explaining the variability in Ln(annual streamflow), Ln(baseflow), or Ln(N loads) for the Des Moines River are listed in Table 3. These p-values were obtained from the stepwise multiple regression analysis. The results show that the current year precipitation followed by the previous year precipitation were the most important variables that explained 69% and 64% of the variability in Ln(annual streamflow) and Ln(annual baseflow), respectively. However, in the case of Ln(annual N loads), only the current year's precipitation was the significant variable and it explained 48% of the variability. The regression results further show that Ln(annual streamflow), Ln(baseflow), or Ln(N loads) were not affected by the previous year soybean area. A comparison of R^2 in Figures 4-5 and Table 3 shows that the previous year's precipitation explained additional 9% of the variability in both Ln(Streamflow) and Ln(baseflow).

Table 3: The p-values of the current year precipitation along with previous two year's precipitation and the previous year soybean area in explaining the variability in Ln(annual streamflow), Ln(annual baseflow), Ln(annual NO_3-N loads), and annual flow-weighted NO_3-N concentrations (FWNC) in the Des Moines River at 2nd Ave Bridge. Dashed boxes indicate non-significant p-values.

Dependent variable	Current Year PPT	Prev Yr PPT	2 Prev Yr PPT	Prev Yr SB area	R^2
	p-value				
Streamflow	1.23E-07	0.006	---	---	0.69
Baseflow	1.04E-06	0.014	---	---	0.64
N-loads	1.00E-05	---	---	---	0.48
FWNC	---	---	---	---	---

The p-values in Table 3 also show that none of the four independent variables (current year precipitation, previous year precipitation, previous 2-year precipitation, or the previous year soybean area) were significant in explaining the variability in FWNC. This is consistent with Fig. 7 which shows a weak second-degree polynomial relationship between FWNC concentration and precipitation. This relationship suggests that as the precipitation increases, there is an increase in FWNC and then a decrease after an annual precipitation of 898 mm. The physical interpretation of the statistical analysis will be that above an annual precipitation of 898 mm, there is a dilution of the available nitrogen for leaching through the soil to the Des Moines River. Even though current year and previous year precipitations are not significant variables in the linear regression, the large scatter in the FWNC data in Fig. 7 is likley due to precipitation history. For example, FWNC in 1991 is greater than the maximum concentration of about 8 mg/L from the polynomial. This is because 1988, 1989 were dry years and some of the nitrogen that did not leach in those two years likely got leached in 1991 (wet year).

Schilling and Lutz (2004) showed that annual, seasonal, and monthly FWNC were significantly related to annual, seasonal, and monthly Ln(baseflow) with corresponding correlation coefficients (R^2) of 0.78, 0.68, and 0.61. Similarly, Schilling (2002) showed that baseflow contributed 61% to 66% of NO_3-N loads in Walnut Creek and Squaw Creek in Iowa. Figure 7 is consistent with these observations considering that Ln(baseflow) is related to precipitation in any given year and the previous year (Table 3). A second-degree plot of FWNC concentration with previous year annual precipitation showed a weak correlation (R^2=0.05) for the Des Moines River. This is expected considering previous year precipitation only explained 9% of the variability in Ln(baseflow).

In Figure 8 are plotted the FWNC versus baseflow. The figure shows that annual FWNC follows a significant second-degree polynomial relationship with annual baseflow i.e., FWNC increases with an increase in baseflow to a value of 230 mm after which there is a decrease with an increase in baseflow. This is also consistent with a second-degree relationship of FWNC with precipitation (Fig. 7) and also that Ln(baseflow) is related to precipitation in the current year as well as with precipitation in the previous year (Table 3).

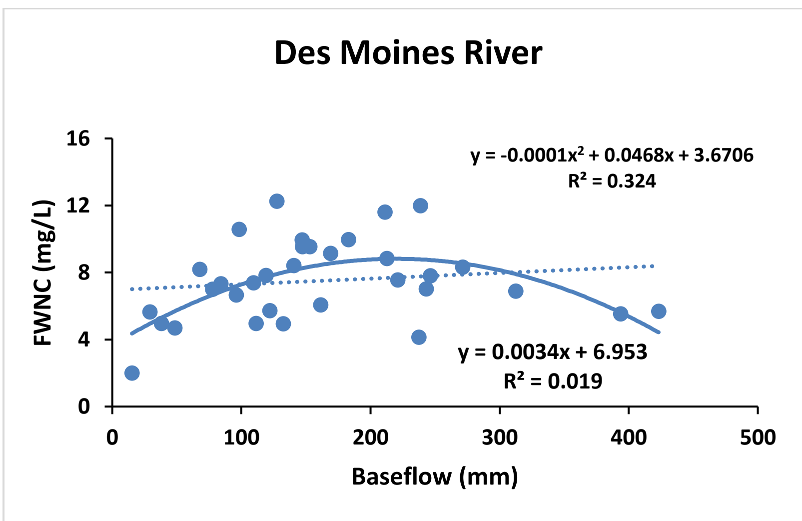


Figure 8: Relationship between annual flow-weighted NO_3-N concentrations (FWNC) and the corresponding baseflow for the Des Moines River at 2nd Ave. Bridge.

Except for a few outliers, annual FWNC concentration in this river generally varied between 4 and 12 mg L^{-1} (Figs. 7 & 8). Since fertilizer use (Fig. 9), cropping system, or other soil and crop management practices are generally similar in back to back years, it suggests that the variation in FWNC is primarily controlled by climatic factors i.e. precipitation (baseflow) differences and a decrease in FWNC over and above a precipitation of 898 mm or baseflow of 230 mm is likely reflecting a dilution effect. A regression analysis of annual FWNC concentration showed that fertilizer N addition as an additional explanatory variable in Eq. (1) contributed little (non-significant) to explaining the variability in FWNC of the Des Moines river from 1987-2001 (Table 1A).

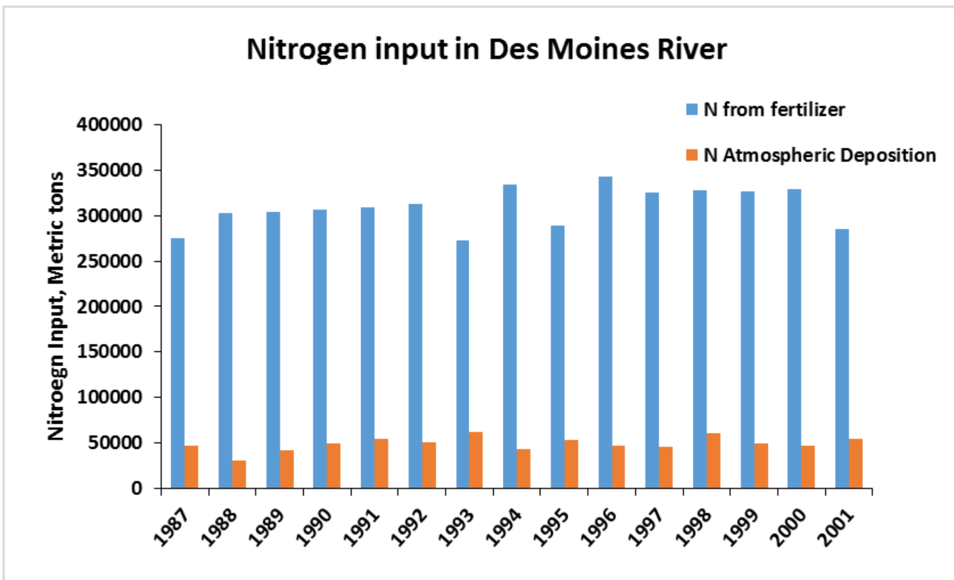


Figure 9: Temporal variation in N addition from fertilizer and atmospheric deposition in the Des Moines River watershed from 1987to 2001 (Ruddy et al., 2006).

Monthly Analysis

Similar to the annual analysis, stepwise multiple regression analysis was also run on monthly values of streamflow, baseflow, N-loads, and FWNC. Like the annual values, monthly values of streamflow, baseflow, and N-loads were also Ln-transformed to make the data normally distributed as well as be consistent with overland and infiltration processes. The explanatory variables in Eq. (2) were the monthly precipitations, previous year precipitation, and the current year and the previous year soybean area. Current year soybean area was included to simulate soybean effects on evapotranspiration whereas previous year soybean area was included to simulate soybean effects on additional N mineralization.

The p-values of selected parameters explaining the variability in monthly Ln(streamflow), Ln(baseflow), Ln(N Loads) and FWNC for the Des Moines River are given in Tables 4 to 7. In general, Ln(streamflow), Ln(baseflow) and Ln(N loads) in any given month were primarily controlled by the precipitation in that month and precipitation in 2-3 months prior to that month. Only for few months, previous year precipitation was important in explaining Ln(streamflow), Ln(baseflow), or Ln(N Load) in the Des Moines River. Previous year soybean area was not a significant variable in explaining variability in Ln(streamflow), Ln(baseflow), and Ln(N loads). The current year soybean area was important in explaining variability in Ln(streamflow) and Ln (baseflow) only in the month of September. There was also no effect of current year soybean area on Ln(N loads). In terms of FWNC, current year soybean was also not a significant variable in explaining its variability.

Table 4: The p-values of current and previous month's precipitation along with previous year's precipitation and current and previous year soybean area in explaining the variability in Ln (monthly streamflow) in the Des Moines River at 2nd Ave Bridge.

Month	Feb PPT	Mar PPT	Apr PPT	May PPT	Jun PPT	Jul PPT	Aug PPT	Sep PPT	Oct PPT	Nov PPT	Dec PPT	Prev Yr PPT	Current Yr SB area	R^2
	p-value													
Apr		0.033	0.015									1.50E-03		0.49
May			4.60E-03											0.30
Jun	0.02	0.018	0.024	1.20E-04	3.90E-05							1.90E-03		0.83
Jul				4.70E-02	9.12E-07									0.65
Aug					4.92E-05	1.60E-03	1.50E-03							0.72
Sep		8.60E-03			8.30E-04	6.00E-03	1.34E-06	1.01E-05					3.80E-03	0.88
Oct						9.60E-03	9.12E-05	1.33E-08	1.59E-06			0.050		0.87
Nov							0.012	3.67E-05	1.68E-06			0.017		0.77
Dec		4.15E-05					8.40E-03	6.18E-06	4.89E-06	8.10E-04		2.55E-05		0.88

Table 5: The p-value of current and previous month's precipitation along with previous year's precipitation and current and previous year soybean area in explaining the variability in Ln (monthly baseflow) in the Des Moines River at 2nd Ave Bridge.

Month	Feb PPT	Mar PPT	Apr PPT	May PPT	Jun PPT	Jul PPT	Aug PPT	Sep PPT	Oct PPT	Nov PPT	Dec PPT	Prev Yr PPT	Current Yr SB area	R^2
	p-value													
Apr		0.021	0.030									4.40E-04		0.51
May			4.40E-04									0.025		0.44
Jun			4.00E-03	3.40E-05								0.017		0.64
Jul				4.30E-03	3.47E-06									0.66
Aug					3.38E-06	3.86E-05	4.80E-02							0.78
Sep					3.10E-03	1.30E-03	3.98E-07	2.00E-03					6.00E-03	0.84
Oct	3.90E-03						3.78E-06	5.12E-09	3.20E-04			0.013		0.88
Nov							0.014	3.49E-06	5.07E-07					0.77
Dec							3.00E-03	4.20E-04	3.86E-05	2.60E-03		0.028		0.77

Table 6: The p-value of current and previous month's precipitation along with previous year's precipitation and current and previous year soybean area in explaining the variability in Ln (monthly N loads) in the Des Moines River at 2nd Ave Bridge.

Month	Jan PPT	Feb PPT	Mar PPT	Apr PPT	May PPT	Jun PPT	Jul PPT	Aug PPT	Sep PPT	Oct PPT	Nov PPT	Dec PPT	Prev Yr PPT	R^2
	p-value													
Apr			3.60E-03	0.022									1.20E-03	0.53
May				8.20E-04										0.32
Jun				1.84E-05	1.07E-05									0.73
Jul					0.015	9.65E-05								0.55
Aug						2.30E-03	7.90E-04							0.58
Sep						0.041	0.011	8.56E-07	0.0032					0.77
Oct	0.027							6.88E-05	8.33E-07	1.30E-04			7.10E-03	0.83
Nov								2.50E-03	1.40E-04	1.39E-05			0.019	0.76
Dec			1.40E-03					0.011	1.20E-03	1.86E-05	3.20E-03		8.70E-04	0.83

Table 7: The p-value of current and previous month's precipitation along with previous year's precipitation and current and previous year soybean area in explaining the variability in monthly FWNC in the Des Moines River at 2nd Ave Bridge.

Month	Apr PPT	May PPT	Jun PPT	Jul PPT	Aug PPT	Sep PPT	Oct PPT	Nov PPT	Dec PPT	Prev Yr PPT	Current Yr SB area	Prev Yr SB area	R^2
	p-value												
Apr	1.69E-04									0.015			0.43
May	8.95E-04												0.32
Jun	1.05E-03											0.042	0.39
Jul		3.84E-04										4.05E-03	0.46
Aug												1.16E-04	0.41
Sep					9.45E-04								0.41
Oct					3.7E-03	0.013	0.050						0.47
Nov					7.78E-04	1.36E-03	1.7E-03			0.034			0.68
Dec						7.30E-03	9.3E-05	2.4E-03					0.56

For most months, previous months precipitation and previous year's precipitation explained over 60% (R^2>0.6) of the variability in Ln(streamflow), Ln(baseflow), and Ln(N loads). Generally, the exceptions were the months of April and May when R^2 varied between 0.3 and 0.5 (Tables 4-5). In the case of FWNC, the current month precipitation or previous 2-3 months precipitation were the only variables that explained a majority of its variability (Table 7). However, there were three months (June, July, and August) when previous year soybean area was also important in explaining variability in FWNC. R^2 values of the monthly FWNC regression generally varied between 0.3 and 0.5. The exceptions were the months of November and December when R^2 values were 0.68 and 0.56. For the month of August, neither the monthly precipitation nor the previous year precipitation was important in explaining FWNC. For this month, FWNC was only related to the area under previous year soybean. This may be partially because tile flow generally stops in the month of August both due to limited precipitation as well as near maximum evapotranspiration (more water and nutrient uptake). This correlation might reflect some contributions of soybean mineralization to FWNC. Overall, low R^2 values for monthly FWNC in Table 7 likely reflect the second-degree polynomial relationship in annual values. In other words, having the same FWNC for the low and high levels of precipitation in any given month will lead to lower R^2 values in a linear relationship like the one used in monthly regression analysis.

Figure 10 shows the monthly variation in FWNC for various months in the Des Moines River. For the months April through December, FWNC were in the range of 2 mg

L^{-1} to 18 mg L^{-1}. In general, the spread of FWNC concentration decreases from April to September and then starts increasing again from October to December. This is likely due to interactions between climate and stage of plant growth. For example in April, there is minimal plant growth (low ET) but also quite a bit of variability in weather conditions in terms of precipitation. The precipitation in April ranged from 25 mm to 160 mm in a 46 year period (1968-2013). Thus, a given amount N in soil (either in residual form or from the addition of fall and spring fertilization) is subject to different amounts of water percolation in different years. Comparatively, in September, plants are near full growth stage with near high ET and a significant amount of N has already been taken up by plants. This along with limited precipitation results in a small amount of variation in FWNC in September.

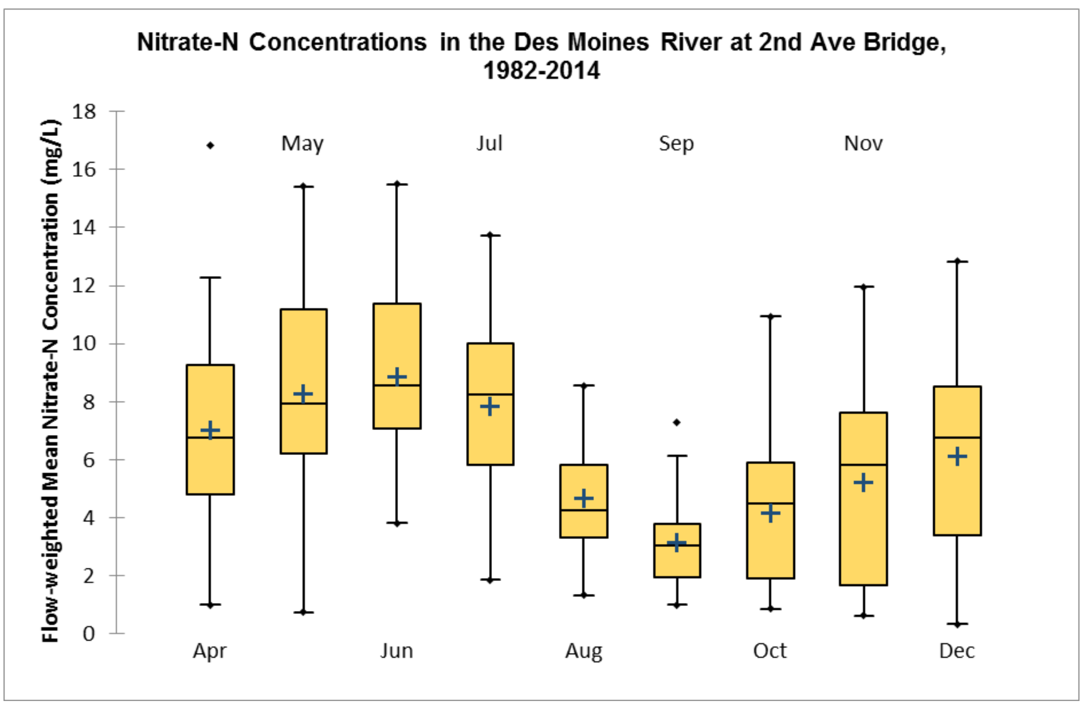


Figure 10: Flow-weighted mean monthly Nitrate-N Concentrations in the Des Moines River at 2nd Ave Bridge. The crosses correspond to the means, dots indicate the minimum and maximum values, central horizontal bars are the medians, lower and upper limits of the box are the first and third quartiles.

Following Schilling and Lutz (2004), we also ran the regression relationship between the monthly FWNC and the corresponding Ln(Q_b); where Q_b represents baseflow (Table 8). For the Des Moines River, R^2 values were lower (R^2=0.16-0.73) than the values (R^2=0.43-0.73) reported by Schilling and Lutz (2004) for the Raccoon River thus indicating a somewhat weaker relationship between the FWNC and Ln(Q_b). Since annual FWNC concentration showed a second-degree relationship with precipitation (Figure 7) and baseflow (Figure 8), we also ran second-degree regression analysis between monthly FWNC and monthly baseflow (Table 9). R^2 values, an indicator of the strength of a relationship, were similar or higher than the R^2 values for monthly FWNC with Ln(baseflow) relationship in Table 8. However, there were two months (August and October) when the second-degree FWNC relationships with baseflow were not significant (Table 9). As previously stated, the second-degree relationship of monthly FWNC with baseflow is also a representation of a dilution effect.

Table 8: Regression equations and correlation coefficients relating FWNC with Ln(Q_b) for various months in the Des Moines River at 2nd Ave. All regression equations were significant.

Month	Regression	R^2
Apr	0.65+2.34 Ln(Q_b)	0.44
May	1.40+2.28 Ln(Q_b)	0.33
Jun	4.52+1.41 Ln(Q_b)	0.21
Jul	4.81+1.06 Ln(Q_b)	0.21
Aug	3.36+0.71Ln(Q_b)	0.16
Sep	2.36+0.68 Ln(Q_b)	0.21
Oct	2.08+1.58 Ln(Q_b)	0.47
Nov	2.07+2.25 Ln(Q_b)	0.65
Dec	2.09+3.28 Ln(Q_b)	0.73

Table 9: Second degree regression equations and correlation coefficients relating FWNC with Q_b for various months in the Des Moines River at 2nd Ave. All but two (August, October) regressions were significant.

Month	Regression	R^2
Apr	$1.92+0.39Q_b-0.0049Q_b^2$	0.49
May	$2.74+0.37Q_b-0.0043Q_b^2$	0.32
Jun	$4.98+0.26Q_b-0.0029Q_b^2$	0.36
Jul	$5.46+0.18Q_b-0.0020Q_b^2$	0.34
Aug	$3.70+0.066Q_b-0.00064Q_b^2$	0.09 NS
Sep	$2.27+0.23Q_b-0.0064Q_b^2$	0.18
Oct	$2.33+0.39Q_b-0.0092Q_b^2$	0.27 NS
Nov	$1.49+0.92Q_b-0.028Q_b^2$	0.58
Dec	$0.85+1.58Q_b-0.064Q_b^2$	0.70

NS = not significant

Similar to annual trend analysis, the FWNC also showed no temporal trends for most months over the study period (Table 10). The only significant temporal trend was in November precipitation (Table 10 and Figure 11). This negative trend showed about 1 cm yr^{-1} decrease in November precipitation.

Table 10: Mann-Kendall trend test on temporal variations in monthly precipitation, streamflow, baseflow, and flow-weighted NO_3-N concentrations (FWNC) for the Des Moines River at 2nd Ave. Bridge. The bold number show a significant temporal trend at α=0.05.

Month	Precipitation		Stream Flow		Baseflow		N-Load		FWC-N	
	P-Value	Sen's Slope	P-Value	Sen's Slope	P-Value	Sen's Slope	P-Value	Sen's Slope	P-Value	Sen's Slope
April	0.57	0.343	0.65	-0.176	0.85	-0.080	0.43	-51.453	0.12	-0.098
May	0.37	0.746	0.73	0.206	0.81	0.105	0.83	11.324	0.88	0.010
June	0.96	-0.075	0.19	0.526	0.25	0.341	0.25	91.972	0.16	0.080
July	0.39	-0.678	0.60	0.301	0.45	0.316	0.49	37.398	0.36	0.054
August	0.43	-0.816	0.51	-0.156	0.27	-0.169	0.27	-16.954	0.55	-0.022
September	0.09	-1.367	0.53	-0.034	0.72	-0.015	0.29	-3.475	0.17	-0.037
October	0.76	-0.349	0.97	0.000	0.86	0.000	0.73	-1.071	0.36	-0.048
November	**0.05**	**-0.997**	0.49	-0.070	0.66	-0.022	0.41	-7.910	0.47	-0.048
December	0.41	0.263	0.33	-0.075	0.44	-0.034	0.64	-4.246	0.78	-0.010

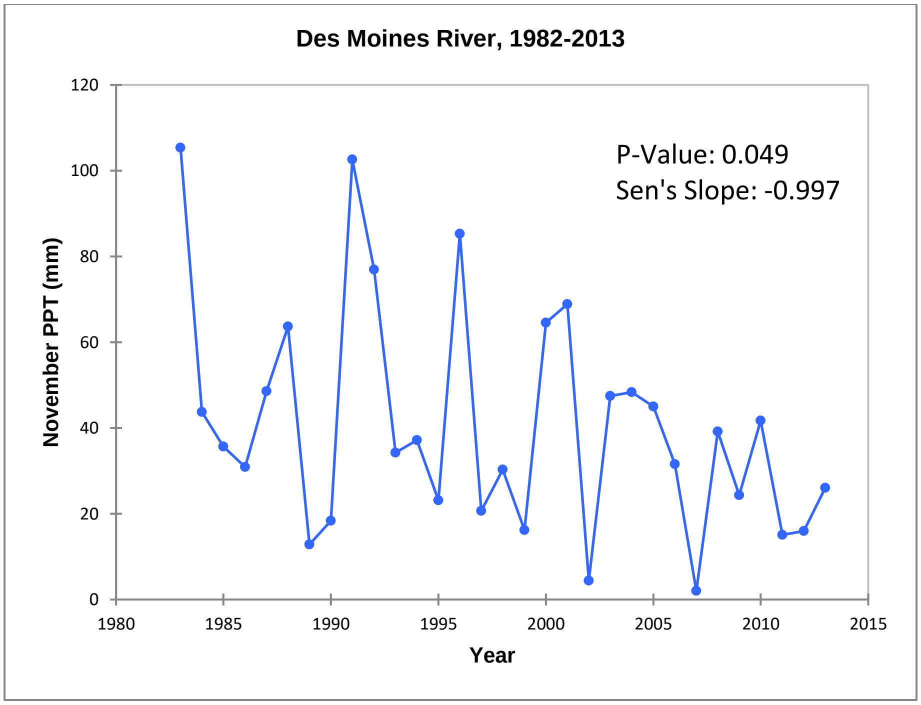


Figure 11: Temporal variation in November precipitation in the Des Moines River at 2nd Avenue Bridge.

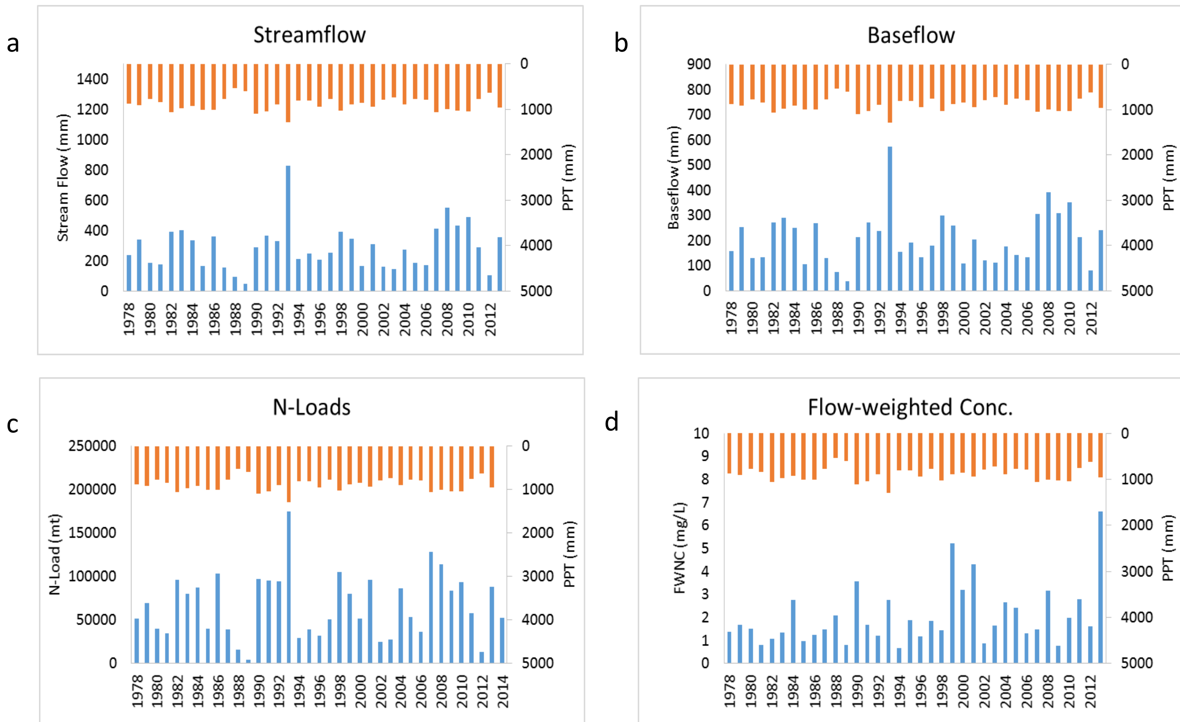
In summary, annual FWNC concentration showed a second-degree variation with precipitation (R^2=0.19)but there was no effect of previous year precipitation or soybean area on annual FWNC. Comparatively, monthly FWNC was related to monthly precipitation (R^2=0.32 to 0.68) in most months, with soybean area in three months (June, July, and August), and previous year precipitation in one month (April) (Table 10). Although fertilizer use data is not available for all the years in the study period, temporal variation of its use from 1987 to 2001 (Fig. 9) show only a slight variation in fertilizer use between years. Similar to above annual analysis, additional regression tests that included the annual fertilizer use as an explanatory variable were also run for the period 1987-2001. This regression analysis showed fertilizer use was not a significant variable in explaining the variability in FWNC or n-loads (Appendix A). This would suggest that under current climate and soil and crop systems, reducing N-loads or FWNC in the Des

Moines River through manipulation of fertilizer use will likely be minimal.

The Iowa River

Annual Analysis

The temporal distribution of the annual precipitation, streamflow, baseflow, NO_3-N-loads, FWNC, for the Iowa River are shown in Fig. 12. The baseflow Index (BFI) for the Iowa River over the study period corresponded to 72%. Like in the Des Moines River, streamflow, baseflow, and N-loads in Iowa River were the highest in 1993, mainly due to an increase in precipitation in that year. Data for 2007 and 2010 also show that consecutive year of higher precipitation results in an increase in the streamflow, baseflow, and N-loads. However, annual FWNC did not show any apparent pattern of change with precipitation as those observed in streamflow, baseflow, and N-loads. Similar to the Des Moines River, Mann-Kendall trend analysis showed no significant temporal trends in the above parameters on an annual basis (Table 11).



Figures 12a-d: Temporal distribution of annual streamflow (Fig. 12a), annual baseflow (Fig. 12b), annual N loads (Fig. 12c), and annual flow-weighted NO_3+NO_2 concentrations (FWNC) (Fig. 12d) for the Iowa River at Wapello and the corresponding precipitation over the watershed.

Table 11: Sen's slope and the p-values of the Mann-Kendall trend in precipitation, streamflow, baseflow, N loads, and FWNC data for the Iowa River at Wapello, IA.

Precipitation		Streamflow		Baseflow		N-Load		FWC-N	
p-Value	Sen's Slope	p-Value	Sen's Slope	p-Value	Sen's Slope	p-Value	Sen's Slope	p-Value	Sen's Slope
0.66	-0.72	0.61	0.92	0.64	0.61	0.77	179.77	0.13	0.02

Except for annual FWNC, annual streamflow, baseflow, and N-loads displayed an exponential relationship with respect to annual precipitation (Figures 13-15). This type of relationship is consistent with physical processes of infiltration and overland flow as discussed earlier in the Des Moines River section. This exponential behavior is also consistent with the log transformation of these variables resulting in their normal distributions. As with Des Moines River, the annual FWNC showed no apparent relationship with precipitation (Fig. 16). Since N-loads are exponentially related to precipitation, it suggests that streamflow is a more dominant variable than the FWNC in the N-loads calculations.

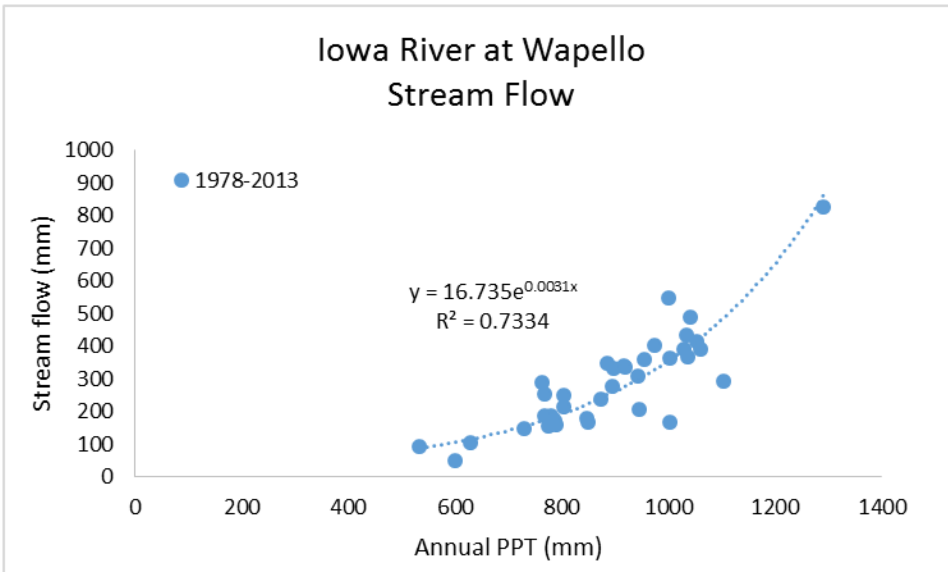


Figure 13: Relationship between annual streamflow for the Iowa River at Wapello and the corresponding precipitation over the watershed

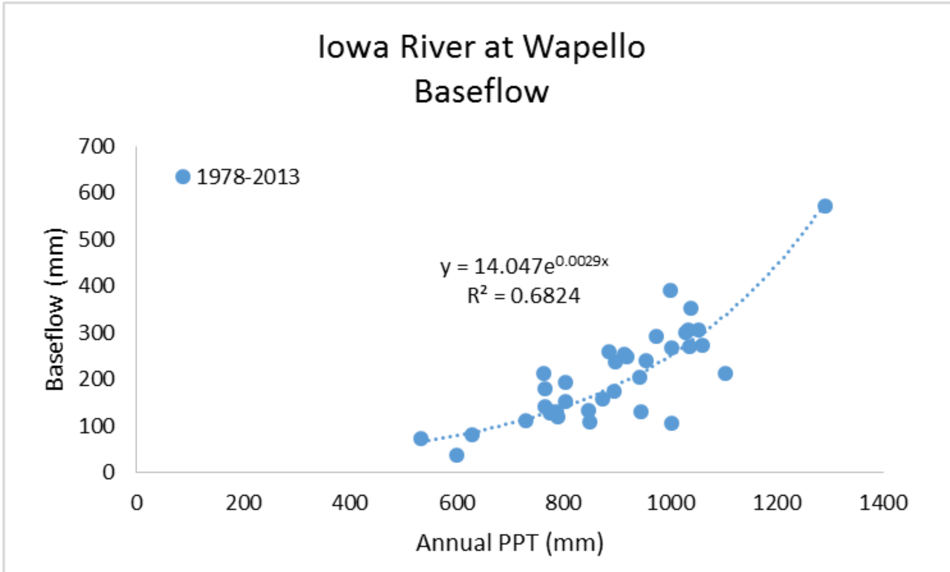


Figure 14: Relationship between annual baseflow for the Iowa River at Wapello and the corresponding precipitation over the watershed

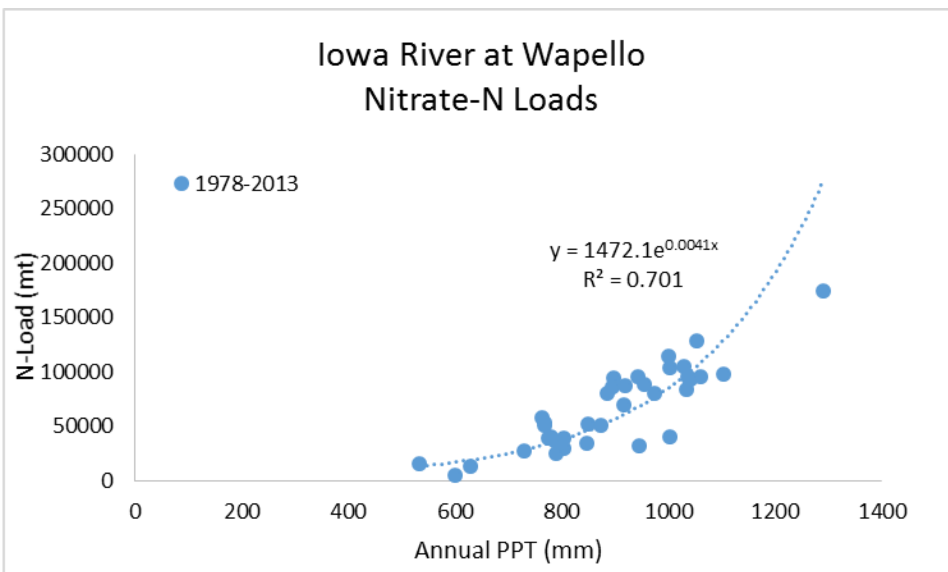


Figure 15: Relationship between annual NO_3-N Loads for the Iowa River at Wapello and the corresponding precipitation over the watershed

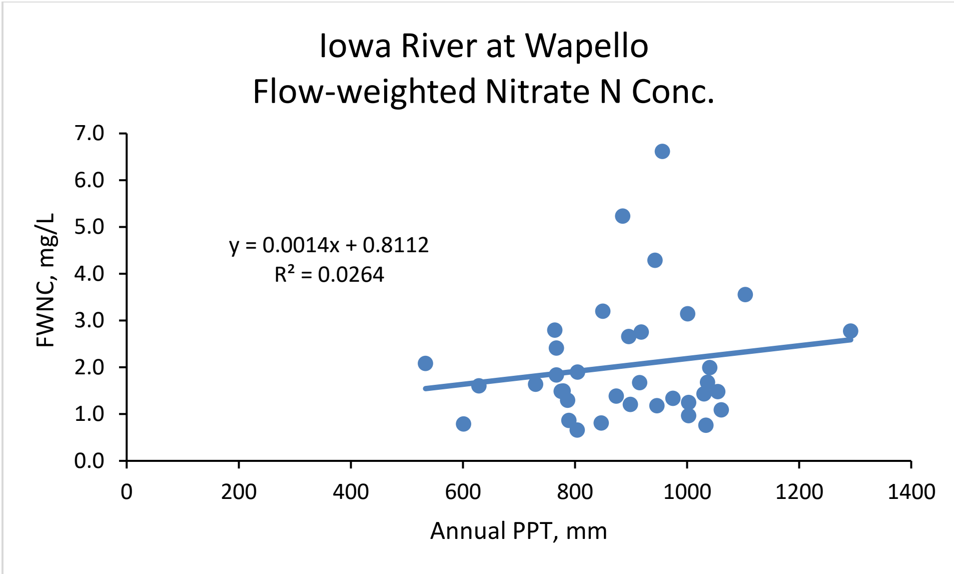


Figure 16: Relationship between annual Flow-weighted Nitrate-N Concentration (FWNC) for the Iowa River at Wapello and the corresponding precipitation over the watershed

The p-values of significant variables explaining the variability in Ln(annual streamflow), Ln(annual baseflow), Ln(annual N loads), and FWNC for the Iowa River as listed in Table 12. These p-values were obtained from a backward stepwise multiple regression analysis. The results show that the current year and previous year precipitation explained 80% and 76% of the variability in Ln(streamflow) and Ln(baseflow), respectively. A comparison of R^2 values in Table 12 with Figs. 13 and 14 suggest that the previous year's precipitation explained 7% and 8% of the variability in Ln(streamflow) and Ln(baseflow), respectively. In terms of Ln(N loads) only the current year precipitation was a significant variable and explained 70% of the variability. The regression analysis further suggested that previous or current year soybean area was not a significant variable in explaining variability in Ln(streamflow), Ln(baseflow), Ln(N-

Load) or FWNC for the Iowa River. Similar to the Des Moines River, there was some relationship between the FWNC concentration and Ln(baseflow) (Fig. 17), but the correlation was weak (R^2=0.07). This is contrary to the observations reported by Schilling and Lutz (2004) of a strong relationship between annual mean N concentrations and the Log(annual baseflow) for the Raccoon River (R^2=0.61). Considering that fertilizer use in Iowa River watershed has been nearly constant (Fig. 18), it would suggest that the variation in FWNC is most likely caused by factors other than changes in LULC or fertilizer management. As an example, fertilizer use in 1993 was less than 1994 but there was higher FWNC in 1993 (2.77 mg L^{-1}) than 1994 (0.66 mg L^{-1}). In these two years, land use changes in terms of tile drainage or area under various crops will be nearly similar. This would suggest that some of the difference in FWNC in these two years are due to differences in weather conditions (more precipitation in 1993). However, over the study period, there was no significant relationship between FWNC and precipitation (Fig. 16).

Similar to Des Moines River, the above annual analysis was also run for the period 1987-2001 with explanatory variables that included the annual fertilizer use. This regression analysis also showed fertilizer use was not a significant variable in explaining the variability in FWNC or N load (Appendix A).

Table 12: The p-values of the current plus previous two year's precipitation and the current and previous year soybean area in explaining the variability in Ln(annual streamflow), Ln(annual baseflow), Ln(annual NO_3-N loads), and annual flow-weighted NO_3-N concentrations (FWNC) in the Iowa River at Wapello, IA.

Dependent variable	Current Year PPT	Prev Yr PPT	2 Prev Yr PPT	Prev Yr SB area	R^2
	p-value				
Stream Flow	7.35E-12	0.002	---	---	0.80
Baseflow	2.23E-10	0.003	---	---	0.76
N-loads	1.96E-10	---	---	---	0.70
FWNC	---	---	---	---	---

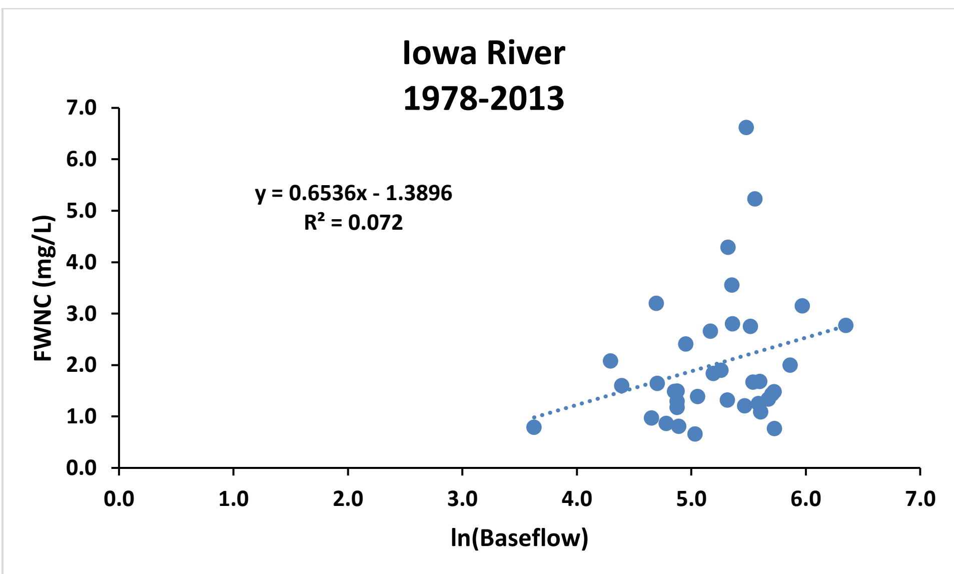


Figure 17: Relationship between annual Flow-weighted Nitrate-N Concentration (FWNC) and Ln(baseflow) for the Iowa River at Wapello.

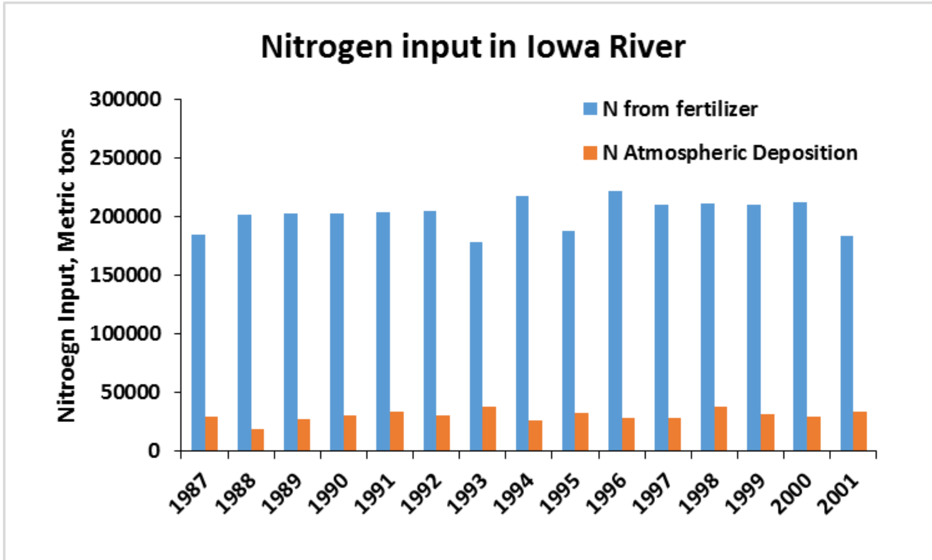


Figure 18: Temporal variation in N input from nitrogenous fertilizer and from atmospheric deposition in the Iowa River watershed. From Ruddy et al., 2006.

Monthly Analysis

The p-values of significant variables explaining the variation in Ln(monthly streamflow), Ln(monthly baseflow), Ln(monthly N loads) and monthly FWNC for the Iowa River are listed in Tables 13-16. Similar to the Des Moines river, precipitation in a given month and 2-3 months prior to the given month were significant in explaining the variability in Ln(streamflow), Ln(baseflow), and Ln(N loads). As expected, previous year's precipitation was also a significant variable in explaining Ln(streamflow), Ln(baseflow), and Ln(N load) early in the season (April through June). This likely reflects the water stored in the soil from previous year's precipitation and its effects on percolation and runoff processes and in turn on streamflow and baseflow. There was no effect of previous year's or present year's soybean area on Ln(streamflow), Ln(baseflow), and Ln(N loads). Except for early in the season (April, May), R^2 values of the regression relationships were generally >0.6 for all three predictor variables.

In terms of monthly FWNC, precipitation in a given month and a month prior were generally the significant variables in explaining its variability. An exception was FWNC in December when previous two year's precipitation was also an explanatory variable. Generally, R^2 values were lower (0.15 to 0.66) for FWNC than the corresponding value for Ln(streamflow), Ln(baseflow), and Ln(N loads).

Table 13: The p-values of current and previous month's precipitation along with previous year's precipitation in explaining the variability in monthly Ln(streamflow) in the Iowa River at Wapello.

Month	Mar PPT	Apr PPT	May PPT	Jun PPT	Jul PPT	Aug PPT	Sep PPT	Oct PPT	Nov PPT	Dec PPT	Prev Yr PPT	R^2
p-value												
April		9.42E-03										0.18
May			3.19E-05								0.03	0.43
June	0.03		6.40E-05	3.87E-04							0.01	0.67
July			4.31E-03	1.64E-04	5.18E-03						0.02	0.73
Aug				2.51E-04	4.79E-05	7.58E-04						0.75
Sept					2.38E-06	1.31E-06						0.74
Oct					1.00E-03	1.16E-04	3.52E-03	2.91E-06				0.79
Nov					1.40E-05	6.23E-03	9.99E-03	7.60E-10	7.57E-06			0.83
Dec						7.21E-04		7.09E-04	1.63E-04	0.03	5.53E-03	0.73

Table 14: The p-values of current and previous month's precipitation along with previous year's precipitation in explaining the variability in monthly Ln(baseflow) in the Iowa River at Wapello

Month	Mar PPT	Apr PPT	May PPT	Jun PPT	Jul PPT	Aug PPT	Sep PPT	Oct PPT	Nov PPT	Dec PPT	Prev Yr PPT	R^2
p-value												
April	6.40E-03										5.87E-03	0.30
May	1.40E-03	7.71E-04									1.37E-03	0.47
June	4.74E-04	3.68E-03	0.02	1.55E-03							1.69E-03	0.73
July	0.04		6.12E-03	5.68E-05	4.04E-02						9.35E-03	0.75
Aug	1.48E-03			8.32E-06	4.22E-06						0.01	0.81
Sept					1.47E-06	2.84E-07						0.76
Oct					3.86E-04	1.45E-03	1.52E-03					0.62
Nov					3.39E-04	0.01		7.81E-07	4.44E-03			0.69
Dec						6.24E-03		2.14E-03	4.31E-04	0.03		0.58

Table 15: The p-values of current and previous month's precipitation along with previous year's precipitation in explaining the variability in monthly Ln(N load) in the Iowa River at Wapello

Month	Mar PPT	Apr PPT	May PPT	Jun PPT	Jul PPT	Aug PPT	Sep PPT	Oct PPT	Nov PPT	Dec PPT	Prev Yr PPT	R^2
p-value												
April	0.01										0.02	0.25
May	0.000974	4.07E-04									0.02	0.45
June	0.03		1.41E-04	1.15E-03							0.03	0.63
July				3.81E-05								0.41
Aug				5.91E-03	1.60E-03							0.51
Sept					9.95E-05	3.58E-04						0.60
Oct					2.60E-04	4.27E-03	1.82E-03	1.80E-05				0.71
Nov					5.88E-05	4.70E-03	5.58E-03	4.46E-09	3.91E-06			0.81
Dec									2.02E-03	2.51E-04		0.39

Table 16: The p-values of current and previous month's precipitation along with previous year's precipitation in explaining the variability in monthly FWNC in the Iowa River at Wapello.

Month	Mar PPT	Apr PPT	May PPT	Jun PPT	Jul PPT	Aug PPT	Sep PPT	Oct PPT	Nov PPT	2 Yr Prev PPT	R^2
p-value											
April											
May	0.02										0.15
June			0.01	0.02							0.36
July				5.53E-04							0.31
Aug				0.02	9.54E-03						0.41
Sept					5.28E-05	2.35E-05					0.66
Oct							5.46E-03	2.54E-04			0.43
Nov							0.01	2.40E-05	8.79E-04		0.55
Dec								4.55E-03	2.30E-05	0.03	0.51

Although the Mann-Kendall test did not show any significant temporal trends in streamflow, baseflow, N-loads, and FWNC on an annual basis (Table 11), there were some significant trends in monthly values of these variables (Table 17). For example, September precipitation decreased by 1.15 cm per year. Comparatively, June streamflow and May N-loads increased by 0.83 cm per year and 275 mt per year, respectively. The FWNC showed mixed temporal trends; increasing in the month of May and June and decreasing in the months of October, November, and December. However, in all these FWNC trends, slopes were relatively small varying from -0.15 mg L^{-1} yr^{-1} to 0.12 mg L^{-1} yr^{-1} (Table 17). Trends found in the later months (Oct, Nov, Dec) may be related to changes in the timing of fertilizer application, the amount of fall-applied fertilizer and even increased fall precipitation. In some Midwestern areas, it is not uncommon to apply fertilizer in the fall months prior to planting in the following year. The downward trends in these months could be due to a shift in N-fertilizer application from fall to spring. Baseflow was the only variable that did not show any trends in the monthly values for the Iowa River.

The relationship between monthly FWNC and Ln(baseflow) (Table 18) showed a weaker relationship (R^2=0.17 to 0.72) compared to the analysis reported by Schilling and Lutz (2004)'s for the Raccoon River (R^2=0.43-0.73). However, the second-degree relationships of the monthly FWNC values with precipitation and baseflow were a bit stronger with R^2 values varying from 0.28 to 0.72 (Table 19). As mentioned previously in the Des Moines River discussion, the second-degree relationship in this analysis is also a representation of the dilution effect from an increase in baseflow and indirectly from an increase in precipitation.

In general, the FWNC in Iowa River ranged from 0.01 to 22 mg L^{-1} (Fig. 19). The spread of FWNC concentration decreases from April to July and then starts increasing again from August to December (Fig. 19). These differences in the spread are likely due to a decrease in precipitation variability in combination with an increase in ET from April to July and thus decreased flow and decreased N loss. Increased spread from August to December may be a reflection of crop maturation with decreasing ET after August and then more precipitation available for downward movement and possibly N losses.

Table 17: Mann-Kendall trend test of temporal variations in monthly precipitation, streamflow, baseflow, and flow-weighted NO_3-N concentrations (FWNC) for the Iowa River at Wapello.

Month	Precipitation		Streamflow		Baseflow		N-Load		FWC-N	
	p-value	Sen's Slope	p-value	Sen's Slope	p-value	Sen's Slope	p-value	Sen's Slope	p-value	Sen's Slope
April	0.123	1.09	0.764	0.08	0.917	-0.03	0.504	65.71	0.293	0.05
May	0.539	0.55	0.063	0.66	0.108	0.35	**0.005**	**275.26**	**0.002**	**0.12**
June	0.301	1.11	**0.048**	**0.83**	0.06	0.42	0.055	255.36	**0.050**	**0.07**
July	0.253	-0.81	0.454	0.21	0.16	0.32	0.105	102.50	0.053	0.06
August	0.127	-1.35	0.496	-0.11	0.69	-0.07	0.443	-20.24	0.426	-0.03
September	**0.044**	**-1.15**	0.231	-0.18	-0.10	-0.10	0.140	-23.33	0.125	-0.06
October	0.513	-0.37	0.200	-0.14	0.20	-0.09	0.147	-40.00	**0.038**	**-0.08**
November	0.102	-0.72	0.068	-0.22	0.15	-0.14	0.053	-74.44	**0.015**	**-0.15**
December	0.276	0.32	0.195	-0.148	0.35	-0.11	0.057	-69.50	**0.020**	**-0.14**

Table 18: Regression equations and correlation coefficients relating FWNC with Ln(baseflow, Q_b) for various months in the Iowa River at Wapello, IA. All regression equations were significant.

Month	Regression	R^2
Apr	$2.32+1.78\ Ln(Q_b)$	0.17
May	$1.45+1.69\ Ln(Q_b)$	0.20
Jun	$-1.39+2.27\ Ln(Q_b)$	0.30
Jul	$-1.39+2.00\ Ln(Q_b)$	0.50
Aug	$-1.93+2.23\ Ln(Q_b)$	0.57
Sep	$-2.36+2.59\ Ln(Q_b)$	0.72
Oct	$-2.96+3.21\ Ln(Q_b)$	0.65
Nov	$-3.03+3.89\ Ln(Q_b)$	0.50
Dec	$-3.04+4.52\ Ln(Q_b)$	0.53

Table 19: Second-degree regression relationships and correlation coefficients between FWNC and baseflow (Q_b) for various months in the Iowa River at Wapello, IA. All regression equations were significant.

Month	Regression	R^2
Apr	$3.19+0.32Q_b-0.0039Q_b^2$	0.28
May	$2.89+0.25Q_b-0.0030Q_b^2$	0.23
Jun	$1.09+0.25Q_b-0.0026Q_b^2$	0.33
Jul	$0.52+0.25Q_b-0.0025Q_b^2$	0.53
Aug	$-0.038+0.30Q_b-0.0025Q_b^2$	0.64
Sep	$-0.16+0.38Q_b-0.0036Q_b^2$	0.72
Oct	$-1.35+0.70Q_b-0.013Q_b^2$	0.70
Nov	$-1.54+0.93Q_b-0.019Q_b^2$	0.56
Dec	$-1.17+1.04Q_b-0.020Q_b^2$	0.58

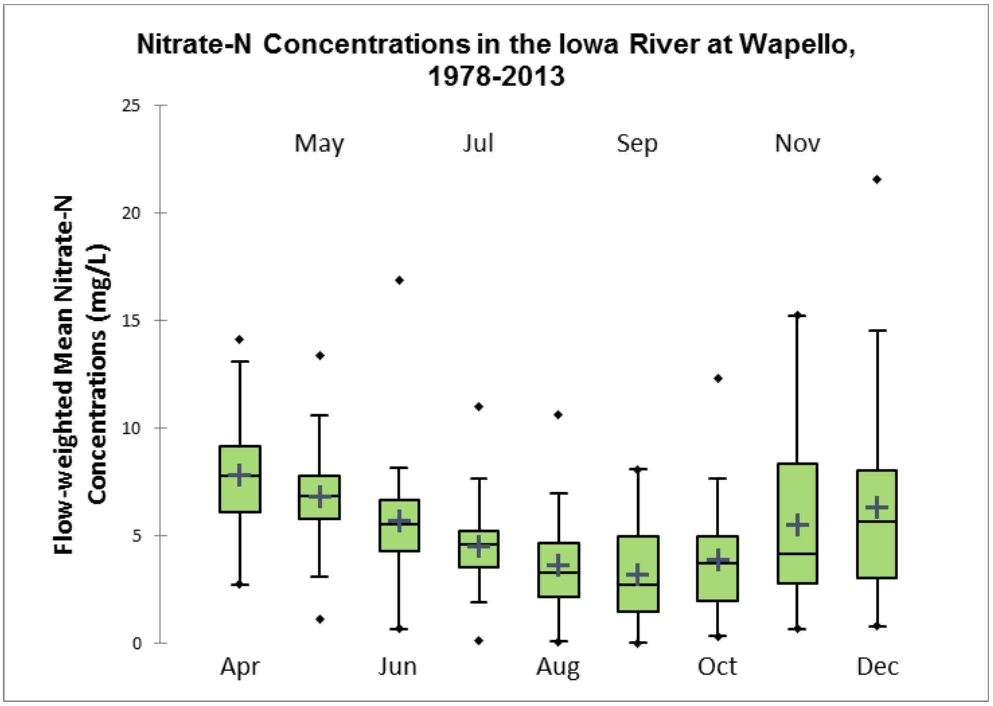


Figure 19: Variations in monthly Flow-weighted Mean Nitrate-N Concentrations in the Iowa River at Wapello, IA. Crosses correspond to the means, dots indicate the minimum and maximum values, central horizontal bars are the medians, lower and upper limits of the box are the first and third quartiles.

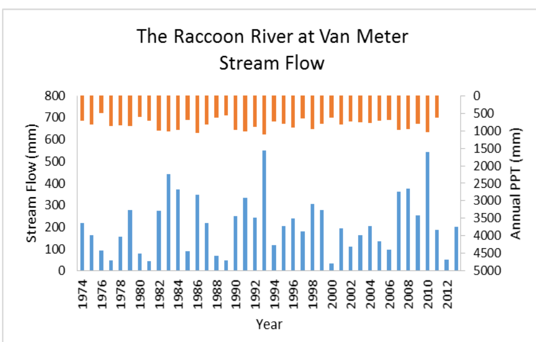
<u>The Raccoon River</u>

Annual Analysis

Temporal distribution of the annual streamflow, baseflow, N-loads, FWNC, along with the annual precipitation for the Raccoon River are similar to those of the Des Moines River and the Iowa River (Fig. 20a-d). For example, streamflow and baseflow in Raccoon River were also higher in 1993 and 2010 due to above average precipitation in these years. The FWNC concentrations were generally lower in 1993 and 2010 likely dilution effects from increased streamflow and baseflow. However, there does not appear to be any consistent trend in FWNC with time or with precipitation. Since N-loads are a result of flow volume and FWNC, N-loads in 1993 and 2010 were higher due to increased streamflow and baseflow (Fig. 20c).

Mann-Kendall trend test of annual streamflow, baseflow, N-load and FWNC showed that there were no significant temporal trends in the above parameters, except in FWNC (p-value=0.047) when Sen's slope showed a yearly increase of 0.08 mg L^{-1} (Table 20). The lack of temporal trends in streamflow, baseflow, and N-loads is likely due to variability in precipitation over time as well as its interactions with crop growth stage. In other words, there are no two similar years when the rainfall amount, intensities and timings are similar at a given crop growth stage.

a



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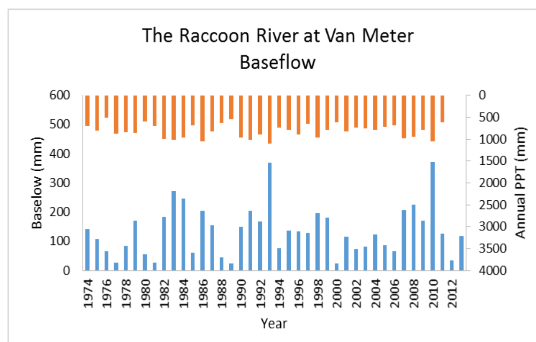
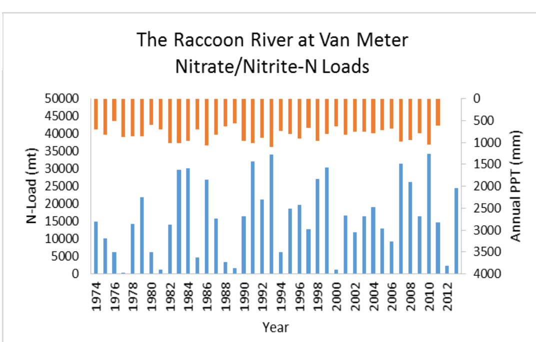


c)



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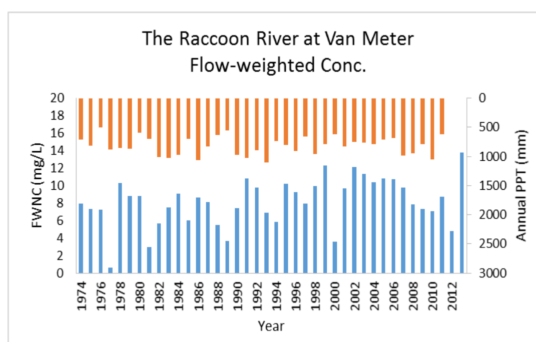

Figures 20a-d: Temporal distribution of annual streamflow (Fig. 20a), annual baseflow (Fig. 20b), annual N loads (Fig. 20c), and annual flow-weighted NO_3+NO_2 concentrations (FWNC) (Fig. 20d) for the Raccoon River at Van Meter and the corresponding precipitation over the watershed.

Table 20: The p-values of Mann-Kendall trend along with Sen's slope in precipitation, streamflow, baseflow, N loads, and FWNC data for the Raccoon River at Van Meter, IA.

Precipitation		Streamflow		Baseflow		N-Load		FWC-N	
p-value	Sen's Slope	p-value	Sen's Slope	p-value	Sen's Slope	p-value	Sen's Slope	p-value	Sen's Slope
0.82	-0.68	0.51	1.24	0.59	0.65	0.13	259.11	**0.05**	0.08

Similar to the Des Moines and the Iowa Rivers, streamflow, baseflow, and N-loads in the Raccoon River also displayed an exponential relationship with precipitation (Figs. 21 to 24). Again, this is consistent with the exponential behavior of infiltration and runoff processes and the statistical requirement of log transformation to simulate a normal distribution. Like in the Des Moines River, FWNC showed a second-degree polynomial relationship with precipitation i.e. FWNC increased with an increase in precipitation but above a precipitation of 942 mm, there was a decrease in FWNC as a result of dilution.

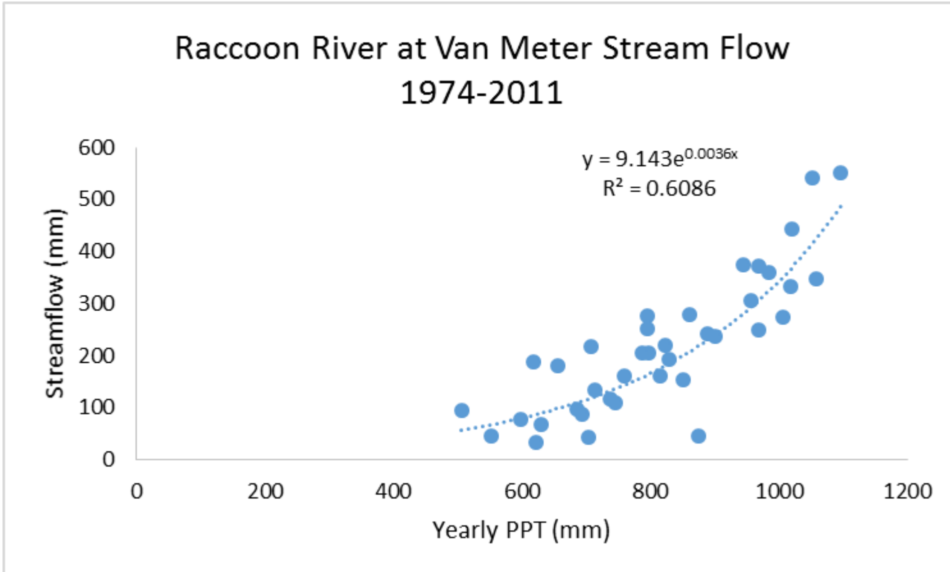

Figure 21: Relationship between annual streamflow for the Raccoon River at Van Meter and the corresponding precipitation over the watershed

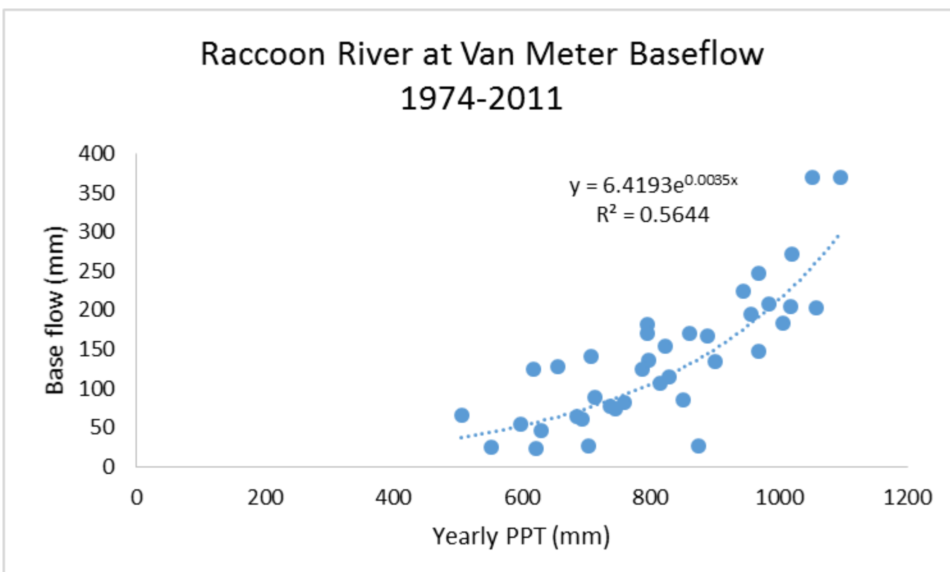

Figure 22: Relationship between annual Baseflow for the Raccoon River at Van Meter and the corresponding precipitation over the watershed

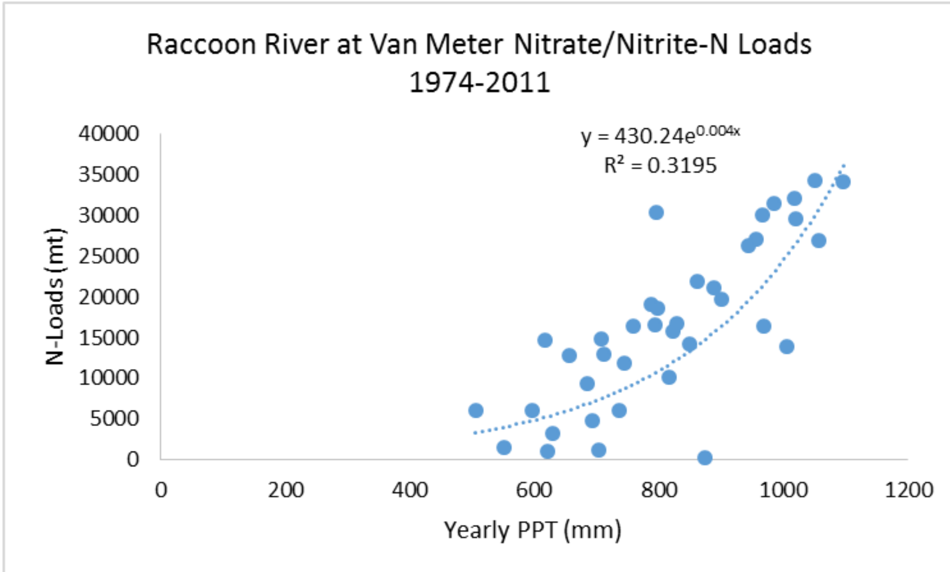

Figure 23: Relationship between annual NO_3-N-loads for the Raccoon River at Van Meter and the corresponding precipitation over the watershed

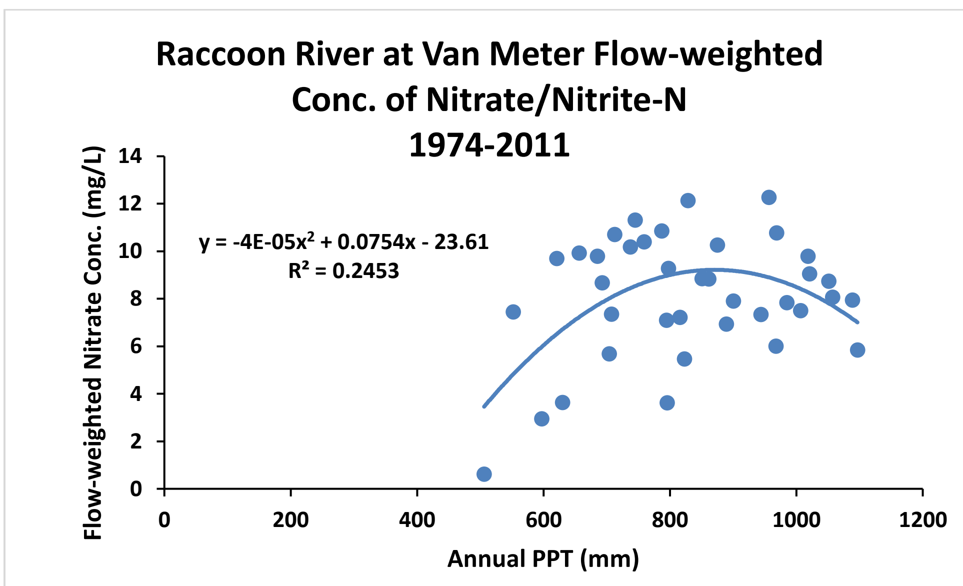

Figure 24: A second-degree polynomial relationship between annual flow-weighted NO_3-N concentrations (FWNC) for the Raccoon River at Van Meter and the corresponding precipitation over the watershed.

The p-values of current and previous year's precipitation along with area under soybean as the explanatory variable for Ln(annual streamflow), Ln(baseflow), or Ln(N loads) in the Raccoon River are listed in Table 21. Similar to the Des Moines River and the Iowa River, these p-values were obtained from a backward stepwise multiple regression analysis. Results show that not only the current year precipitation but also the previous year precipitation were significant variables in explaining the variability in Ln(streamflow), Ln(baseflow), and Ln(N loads). For the annual values, the current year and previous year precipitations explained 73%, 72%, and 49% of the variability in Ln(streamflow), Ln(baseflow) and Ln(N loads), respectively (Table 21). A comparison of R^2 in Figures 21-24 and Table 20 shows that the previous year's precipitation explained 12% and 16% of the variability in Ln(streamflow) and Ln(baseflow), respectively. Regression analysis of the annual values also showed that Ln(streamflow), Ln(baseflow) and Ln(N loads) were not affected by the current or previous year area under soybean production.

Similar to the Des Moines River and the Iowa River, regression analysis also showed that annual FWNC was not linearly related to the annual precipitation or the current or previous year soybean area. However, as shown in Fig. 24, it is a non-linear function of precipitation. The absence of soybean as a significant variable suggests that cropping system likely has a minimal to no effect in controlling FWNC in the Raccoon River. Although fertilizer use in the Raccoon River watershed was not part of the explanatory variables in the regression, limited N fertilizer use data in the watershed from 1987 to 2001 (Fig. 25) shows that annual fertilizer use was nearly similar from year to year. A separate regression analysis for the period 1987-2001 using the above explanatory variables as well as the annual fertilizer use showed fertilizer use and soybean area were not a significant variable in explaining the variability in FWNC, streamflow, baseflow or N loads (Tables 9.A-12.A). This further strengthens the finding that FWNC and N loads are mainly controlled by other factors including climate under the current cropping and management systems. Thus it will be difficult to manage N loads in Raccoon River by just manipulating the fertilizer rate in the basin.

Table 21: The p-values of the current year precipitation along with previous year's precipitation and the soybean area in explaining the variability in Ln(annual streamflow), Ln(annual baseflow), Ln(annual NO_3-N loads), and annual flow-weighted NO_3-N concentrations (FWNC) in the Raccoon River at Van Meter.

Dependent variable	Current Year PPT	Prev Yr PPT	2 Prev Yr PPT	Prev Yr SB area	R^2
	p-value				
Stream Flow	1.45E-10	7.85E-04	---	---	0.73
Baseflow	5.38E-10	2.08E-04	---	---	0.72
N-loads	3.82E-05	2.92E-03	---	---	0.49
FWNC	---	---	---	---	---

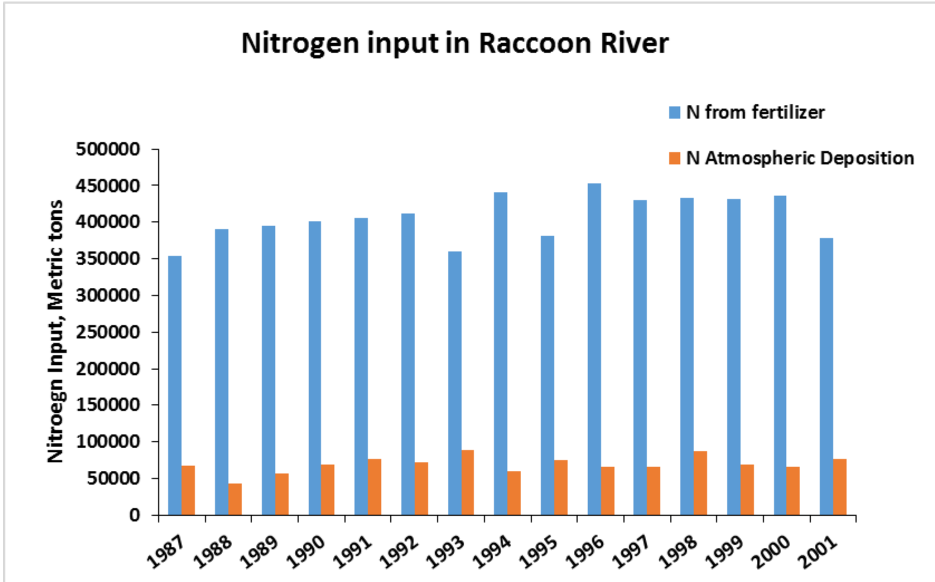

Figure 25: Temporal variation in N input from applied fertilizer and atmospheric deposition in the Raccoon River watershed.

Monthly Analysis

The p-values of Mann-Kendall trend test (Table 22) showed that there was no trend in monthly values of precipitation, streamflow, or FWNC for the Raccoon River. Baseflow had a significant increase in the month of June whereas N Loads had a significant increase in the months of May and June. The significant increase in June N loads could be due to an increase in June baseflow.

Table 22: Monthly Sen's slope and the p-values of the Mann-Kendall trend in precipitation, streamflow, baseflow, N loads, and FWNC data for the Raccoon River at Van Meter, IA.

Month	Precipitation		Stream Flow		Baseflow		N-Load		FWNC	
	p-value	Sen's Slope	p-value	Sen's Slope	p-value	Sen's Slope	p-value	Sen's Slope	p-value	Sen's Slope
April	0.47	0.395	1.00	0.001	0.82	-0.003	0.78	5.307	0.44	0.039
May	0.41	0.623	0.15	0.476	0.26	0.238	**0.02**	**87.583**	0.08	0.099
June	0.41	0.754	0.06	0.752	**0.03**	**0.521**	**0.03**	**94.688**	0.12	0.095
July	0.74	0.260	0.51	0.103	0.24	0.163	0.30	0.018	0.11	0.083
August	0.41	-0.959	0.96	0.000	0.44	0.040	0.80	1.212	0.86	-0.005
September	0.38	-0.427	0.45	-0.035	0.97	0.000	0.35	-0.642	0.29	-0.029
October	0.63	-0.343	0.53	-0.030	0.62	-0.014	0.42	-1.505	0.30	-0.046
November	0.23	-0.426	0.58	-0.028	0.85	0.000	0.59	-1.604	0.70	-0.026
December	0.41	0.275	0.50	-0.044	0.50	-0.027	0.86	-0.673	0.54	0.034

The p-values of significant variables in the stepwise regression analysis showed that monthly Ln(streamflow), Ln(baseflow), and Ln(N loads) for the Raccoon River were controlled by the precipitation in that month and precipitation at least one month prior (Tables 23 to 25). For the case of Ln(Streamflow) in April-July and for the case of Ln(Baseflow) and Ln (N Loads) in April-August, previous year's precipitation was also a significant variable in explaining their variability. Previous year soybean area was only effective in explaining the variability in: (1) Ln(streamflow) for the month of October, (2) Ln(baseflow) for the month of June, and (3) Ln(N loads) for the month of May. Except for the month of December, current and previous months precipitation and previous year's precipitation explained over 65% (R^2 to vary from 0.65 to 0.78) of the variability in Ln(streamflow). Comparatively, current and previous month's precipitation and previous year's precipitation explained over 50% (R^2>0.5) of the variability in Ln(baseflow) and Ln(N loads). The exceptions were Ln(baseflow) in December and N-loads in November and December when R^2 values were less than 0.5 (Tables 23 to 26).

For FWNC, there were only a few months when monthly precipitation was a significant variable and explained some of its variability (Table 26). Also, there were only two months (May and June) when the previous soybean area was a significant (R^2 values of 0.21 – 0.40). This could be an indication of soybean residue mineralization (Jones et al., 2016). Similar to Schilling and Lutz (2004) analysis, there was some relationship between monthly FWNC and Ln(baseflow) (Table 27). However, R^2 values in the current study (0.23-0.63) were lower than those (0.43-0.73) reported by Schilling and Lutz (2004) for the Raccoon River. This difference could be due to the differences in the time period (1974-2011) covered in this study relative to Schilling and Lutz (2004) who used the data from 1974-2000. Some of these differences could also be in the use of mean concentrations in the regression analysis. The Schilling and Lutz (2004) study used the monthly mean nitrate concentrations, whereas in this study we used FWNC. An additional difference could be in the estimation of baseflow values. We used USGS PART (Rutledge, 1998) program to calculate baseflow whereas Schilling and Lutz, (2004) used hydrograph separation method of Sloto and Crouse, (1996). Considering that annual FWNC was related to annual precipitation with a second-degree relationship, we also ran a second-degree relationship of monthly FWNC concentration with monthly baseflow (Table 28) and found that R^2 values were slightly higher in some months and slightly lower in other months.

Figure 26 shows the monthly variation in FWNC for the months of April to December in the Raccoon River at Van Meter. The monthly FWNC ranges from 0.03 mg L^{-1} to 20 mg L^{-1} and are similar to the Des Moines and the Iowa rivers values i.e. the spread in FWNC decreases from May to September and starts increasing again from October to December. This difference in the spread is most likely due to a decrease in precipitation combined with an increase in ET from May through September and then increase in precipitation and decrease in ET from October to December.

Table 23: The p-values of current and previous month's precipitation along with previous year's precipitation and soybean area in explaining the variability in Ln (monthly streamflow) in Raccoon River at Van Meter, IA.

Month	Jan PPT	Feb PPT	Mar PPT	Apr PPT	May PPT	Jun PPT	Jul PPT	Aug PPT	Sep PPT	Oct PPT	Prev Yr PPT	SB area	R^2
							p-value						
April	0.010		0.0024	1.07E-05							7.00E-05		0.71
May				5.83E-03	1.39E-06						5.98E-03		0.65
June					2.35E-07	1.16E-07					4.91E-05		0.78
July					4.81E-04	4.38E-05	5.59E-05				9.94E-04		0.76
Aug						4.95E-04	8.66E-05	5.43E-06					0.72
Sept							5.50E-07	2.43E-05	2.24E-03				0.74
Oct					0.022		1.78E-05	1.27E-05	9.47E-06	1.06E-07	0.013	0.011	0.86
Nov	5.14E-03						7.51E-05		7.65E-03	1.85E-06			0.68
Dec										6.39E-03			0.20

Table 24: The p-value of current and previous month's precipitation along with previous year's precipitation and soybean area in explaining the variability in Ln (monthly baseflow) in the Raccoon River at Van Meter, IA.

Month	Jan PPT	Feb PPT	Mar PPT	Apr PPT	May PPT	Jun PPT	Jul PPT	Aug PPT	Sep PPT	Oct PPT	Prev Yr PPT	SB area	Prev Yr SB area	R^2
							p-value							
April	9.40E-04		5.40E-03	9.23E-05							1.60E-04			0.67
May				5.73E-04	5.76E-05						2.96E-04			0.66
June				0.038	9.09E-07	4.66E-06					4.74E-05	0.049	0.049	0.79
July					1.33E-04	5.56E-06	2.41E-03				3.18E-04			0.76
Aug					5.48E-04	1.13E-04	1.91E-05	5.38E-03			1.32E-03			0.79
Sept							1.63E-03	1.38E-03						0.73
Oct							3.90E-06	6.96E-05	2.14E-04	2.97E-04				0.76
Nov							2.79E-04			3.2163E-05				0.54
Dec							2.60E-03			4.71E-03				0.36

Table 25: The p-value of current and previous month's precipitation along with previous year's precipitation and soybean area in explaining the variability in Ln (monthly N loads) in the Raccoon River at Van Meter, IA.

Month	Jan PPT	Feb PPT	Mar PPT	Apr PPT	May PPT	Jun PPT	Jul PPT	Aug PPT	Sep PPT	Oct PPT	Prev Yr PPT	Prev Yr SB area	R^2
p-value													
April	0.024		0.049	1.90E-04							4.90E-04		0.60
May				0.029	3.02E-03						5.55E-03	0.035	0.53
June					4.20E-04	4.16E-03					7.89E-04		0.53
July					3.56E-04	3.70E-03	0.047				2.94E-04		0.63
Aug					1.83E-04		1.16E-04	0.014			0.034		0.61
Sept							1.81E-04	3.27E-04					0.53
Oct								4.32E-03	1.23E-03	1.43E-03			0.52
Nov									2.60E-02	2.67E-05	0.02532925		0.47
Dec										2.31E-03	0.035636		0.28

Table 26: The p-value of current and previous month's precipitation along with previous year's precipitation and soybean area in explaining the variability in monthly FWNC in the Raccoon River at Van Meter, IA.

Month	Apr PPT	May PPT	Jun PPT	Jul PPT	Aug PPT	Sep PPT	Prev Yr SB area	R^2
p-value								
April	4.11E-04							0.31
May	3.16E-04						1.74E-03	0.42
June							5.03E-03	0.21
July								
Aug								
Sept				6.47E-03	1.83E-03			0.40
Oct						2.9E-02		0.13

Table 27. Regression equations and correlation coefficients relating FWNC with Ln(baseflow, Q_b) for various months in the Raccoon River at Van Meter. All regressions were significant.

Month	Regression	R^2
Apr	$1.70+2.43\ Ln(Q_b)$	0.47
May	$2.24+2.49\ Ln(Q_b)$	0.36
Jun	$5.42+1.61\ Ln(Q_b)$	0.23
Jul	$3.63+1.92\ Ln(Q_b)$	0.27
Aug	$1.14+1.73Ln(Q_b)$	0.44
Sep	$0.27+2.18\ Ln(Q_b)$	0.63
Oct	$1.14+2.67\ Ln(Q_b)$	0.57
Nov	$2.15+2.60\ Ln(Q_b)$	0.48
Dec	$4.29+2.50\ Ln(Q_b)$	0.40

Table 28: Second-degree regression relationships and correlation coefficients between FWNC and baseflow (Qb) for various months in the Raccoon River at Van Meter. All regressions were significant.

Month	Regression	R^2
Apr	$3.02+0.47Q_b-0.0071Q_b^2$	0.43
May	$3.82+0.42Q_b-0.0055Q_b^2$	0.33
Jun	$6.20+0.34Q_b-0.0047Q_b^2$	0.27
Jul	$5.44+0.27Q_b-0.0029Q_b^2$	0.21
Aug	$1.66+0.44Q_b-0.0069Q_b^2$	0.42
Sep	$0.13+0.78Q_b-0.020Q_b^2$	0.69
Oct	$1.12+0.90Q_b-0.023Q_b^2$	0.55
Nov	$1.53+1.15Q_b-0.039Q_b^2$	0.52
Dec	$2.81+1.57Q_b-0.070Q_b^2$	0.48

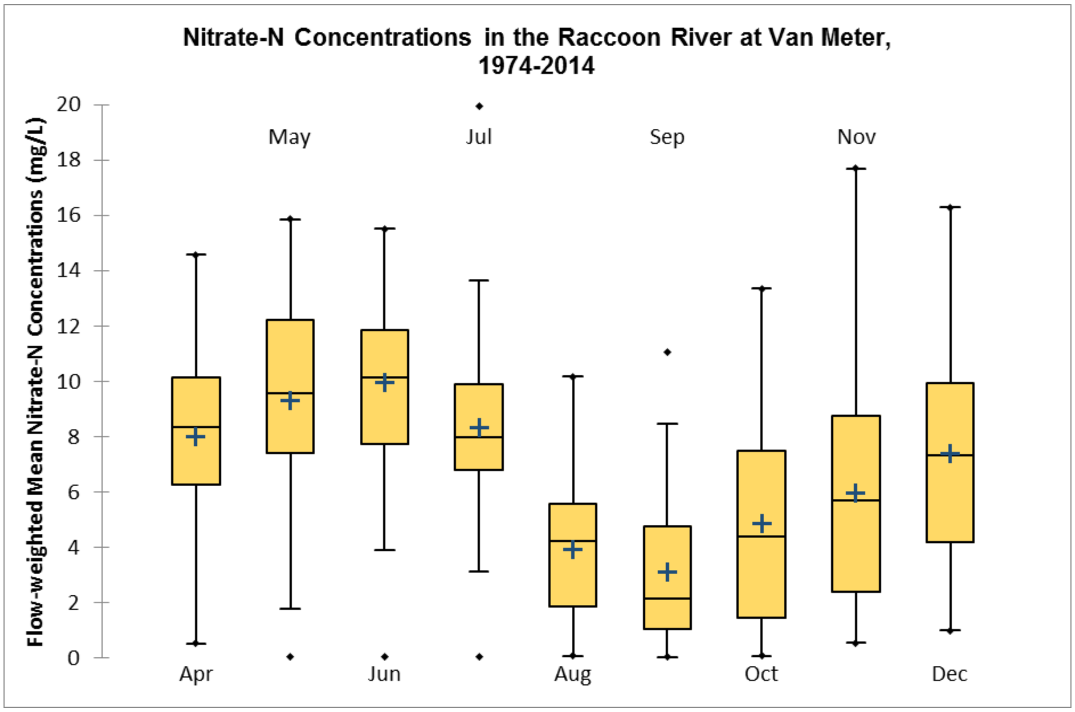

Figure 26: Monthly Flow-weighted Mean Nitrate-N Concentrations in the Raccoon River at Van Meter, IA. Crosses correspond to the means, dots indicate the minimum and maximum values, central horizontal bars are the medians, lower and upper limits of the box are the first and third quartiles.

Combined Annual Analysis

Considering all three rivers had similar exponential relationships for streamflow, baseflow, and N-load with precipitation, we wanted to further explore if there was any commonality in these relationships among three rivers. Since streamflow and baseflow are expressed on a unit area basis, we also converted N-loads to unit area basis (N Yield=annual N-load/watershed area). Figures 27-29 are plots of annual streamflow, baseflow, and N yield as a function of annual precipitation for three combined rivers; the Des Moines River, the Iowa River, and the Raccoon River. All three plots show that irrespective of the period covered for each of the rivers in this study, a single relationship of annual streamflow, baseflow, and N yield as a function of annual precipitation applies. To further test if these relationships improve when previous year(s) precipitation and soybean area are incorporated into the regression, we ran backward stepwise regression on Ln(streamflow), Ln(baseflow), and Ln(N yield) with precipitation in the current year, precipitation in two previous years, and soybean area. In Table 29 are summarized the p-values of the significant variable describing these relationships. The corresponding regression coefficients and standard errors are given in Table 30. These regression coefficients show that Ln(streamflow), Ln(baseflow) and Ln(N yield) are generally a function of precipitation in a given year and a previous year. Furthermore, these relationships are nearly the same for all three rivers. The coefficient of determination (R^2) of Ln(streamflow), Ln(baseflow) and Ln(N yield) were 0.74, 0.70 and 0.54, respectively. Although R^2 for Ln(N yield) are lower than those of Ln(streamflow) and Ln(baseflow), they are still reasonable considering the three rivers represent large watersheds in somewhat different geographical landscapes of Iowa. Potentially, there are some differences in N fertilizer use, the timing of its application, and relative distribution of inorganic and organic fertilizer use among these watersheds. If these relationships hold for other rivers in Iowa and the Upper Midwest, this suggests that variation in N losses from different watersheds is primarily controlled by precipitation and to a much lesser extent by soil and crop management practices such as the timing of N application, crop type, N rate.

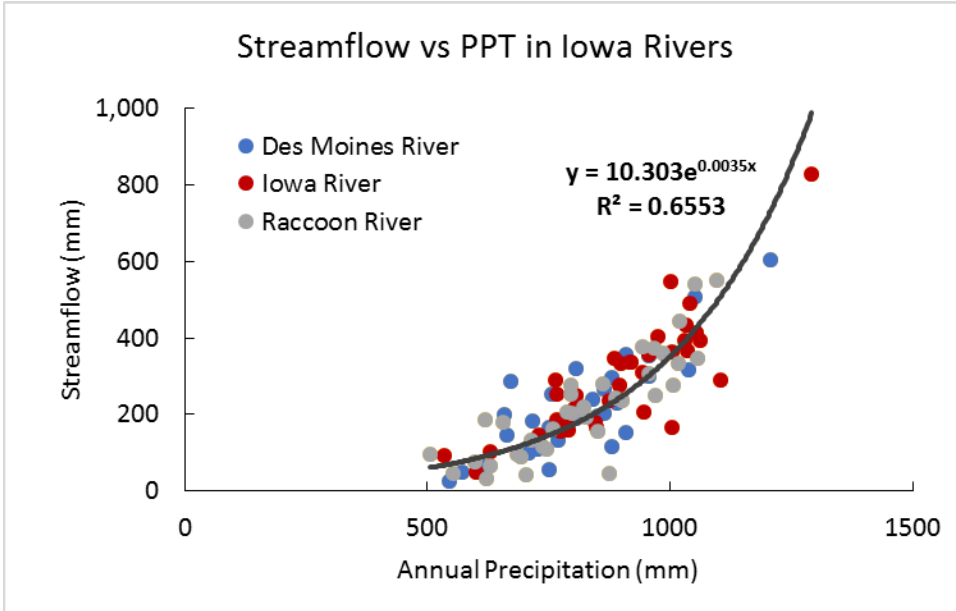

Figure 27: Combined annual streamflow as a function of annual precipitation for three rivers; the Des Moines River, the Iowa River, and the Raccoon River

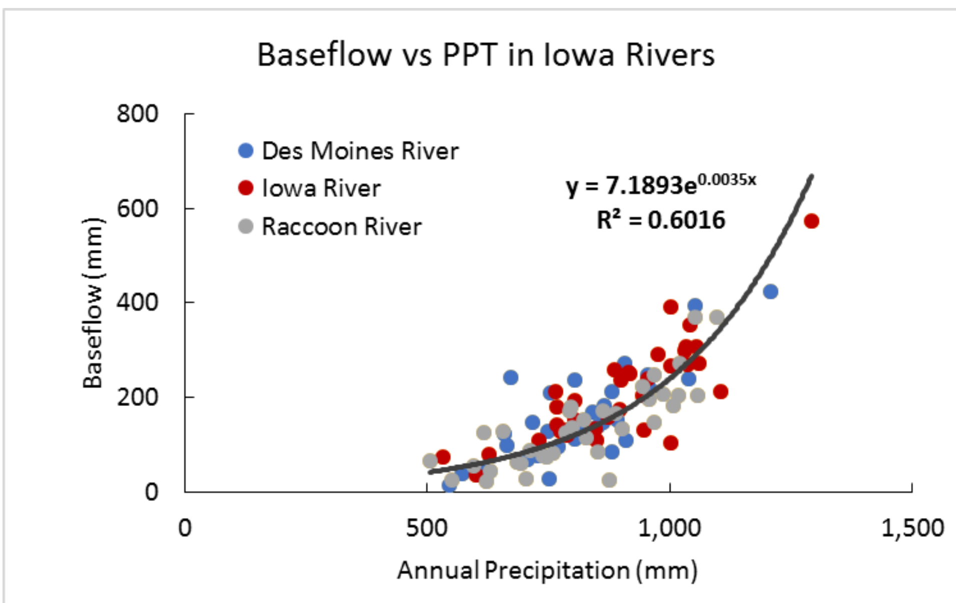

Figure 28: Combined annual baseflow as a function of annual precipitation for three rivers; the Des Moines River, the Iowa River, and the Raccoon River

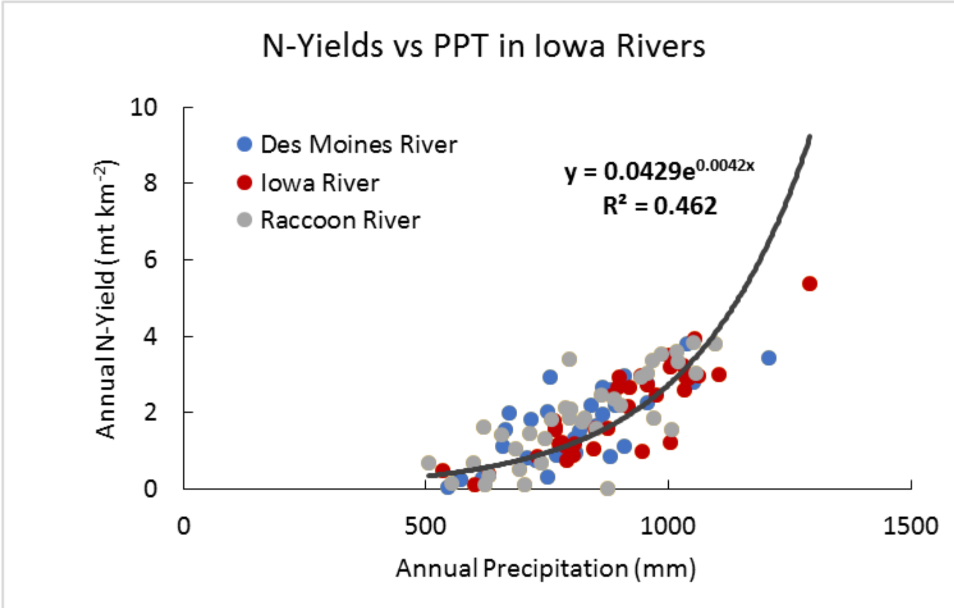

Figure 29: Combined annual N-yield as a function of annual precipitation for three rivers; the Des Moines River, the Iowa River, and the Raccoon River

Table 29: The p-values of the current year precipitation along with previous year's precipitation in explaining the variability in Ln(annual streamflow), Ln(annual baseflow), and Ln(annual NO_3-N yield) for combined data from three rivers in Iowa.

Dependent Variable	Current Yr PPT	Prev Yr PPT	R^2
	p-value		
Streamflow	1.89E-27	1.20E-07	0.74
Baseflow	5.74E-24	1.03E-07	0.70
N-Yield	1.86E-15	1.16E-04	0.54

Table 30: Regression coefficients and the corresponding standard errors for the relationship between Ln(streamflow), Ln(baseflow), and Ln(N yield) for combined data from three Iowa rivers with the current year (β_1) and the previous year precipitation (β_2).

Y	β_0†	β_1	β_2	R^2
	--------- Values *(Standard Error)* --------			
Streamflow	1.37	3.37E-03	1.29E-03	0.74
	(0.25)	*(2.2E-04)*	*(2.3E-04)*	
Baseflow	0.9	3.30E-03	1.40E-03	0.70
	(0.28)	*(2.5E-04)*	*(2.5E-04)*	
N-Yield	-4.41	4.00E-03	1.70E-03	0.54
	(0.48)	*(4.2E-04)*	*(4.2E-04)*	

†$Ln(Y)=\beta_0+\beta_1*P_1+\beta_2*P_2$

DISCUSSION AND CONCLUSIONS

Eutrophication of water bodies as a result of nutrient enrichment is a global problem (Sinha et al., 2017). Although phosphorus inputs are the leading cause of freshwater eutrophication, nitrogen inputs are the main reason for eutrophication of coastal marine ecosystems (Howarth and Marion, 2006; Sinha et al., 2017). A prominent example of coastal water eutrophication and resulting hypoxic conditions in the United States is the northern Gulf of Mexico (Rabalais et al., 2002a, b). It is well established that the primary cause of this hypoxic condition is the nitrogen input from agricultural lands mainly in the Midwestern United States (Goolsby et al., 2001). Iowa is one of the leading agricultural states in the Midwest and thus its rivers are a major source of nitrogen input to the Mississippi River and then to the northern Gulf of Mexico (Goolsby et al., 2001). Regression analysis of streamflow, baseflow, N-loads and FWNC of three Iowa rivers (the Des Moines River, the Iowa River, and the Raccoon River) in this study showed that increases in N-loads are mainly due to increases in streamflow and baseflow which in turn are controlled by increased precipitation in the corresponding watersheds. In the case of annual analysis, increased streamflow and baseflow were not only affected by the annual precipitation in a given year but also by precipitation in the previous year. Previous year precipitation reflects the lack or excess presence of stored water in the soil and its consequences both in terms of overland flow, infiltration, and percolation processes. In all three cases, Ln(streamflow), Ln(baseflow), and Ln(N loads) were linearly related to precipitation. In other words, per unit change in precipitation leads to an exponential change in streamflow, baseflow, and N-loads. Considering there has been a 10-15% increase (50-100 mm) in annual precipitation in recent years and this trend is forecast to continue (USGCRP, 2017) would suggest that streamflow, baseflow, and N-loads will continue to exponentially increase under the current climate change scenarios.

Since precipitation appears to be the main driver of increased baseflow and a substantial amount of N is lost with baseflow, one of the ways to reduce N-loads in this river will be is to control tile flow to streams. This control could be through holding water in ponds and releasing it later in the season, or use of surface inlets that lessen the percolation of water through soil and thus lessen N loss. However, both these options have pitfalls. For example, holding water in upland (natural or engineered storage) will affect the water table, thus making tile drainage less effective. Holding water in upland can also affect the seepage processes thus enhancing bank sloughing depending upon where the holding ponds are constructed and whether or not they are lined with an impermeable material. This practice will also be expensive and will disfigure a significant portion of the landscape. On the use of surface inlets to decrease tile flow, there will be an increase in overland flow and thus an increase in sediment and sediment-attached P loads to the river.

In terms of annual FWNC, regression analysis showed a first degree (the Iowa River) or a second degree (the Des Moines and Raccoon Rivers) relationships with annual precipitation. However, the correlation coefficients were relatively small. Annual

FWNC were generally higher for the Des Moines River (2-12 mg L^{-1}) and the Raccoon River (0.6-14 mg L^{-1}) and low for the Iowa River (0.7 to 7 mg L^{-1}). This likely reflects the landscape conditions of the watersheds. The Iowa River watershed has a more rolling topography and thus more inputs of nitrogen deficient overland flow to the river leading to a dilution effect. Also, there may be less tile drainage in this watershed, and thus less N input to the river because of medium to high relief of the Iowa River watershed. The second-degree relationship between the FWNC and precipitation in the Des Moines River and the Raccoon River suggested that precipitation above some level (898 mm for Des Moines and 942 mm for the Raccoon River) leads to a decrease in FWNC; likely a dilution effect.

In the regression analysis of annual data for all four variables (streamflow, baseflow, N-loads, and FWNC), soybean area was not a significant variable. This is contrary to the conclusions of Schilling (2003), Schilling and Libra (2000), Schilling et al. (2004) and Jones et al. (2016) who suggested that increased N-loads are due to increased adoption of soybeans in the cropping system. Schilling and co-workers have reasoned that later planting of soybean leads to less ET earlier in the season and thus more baseflow and more N loss. They have also reasoned faster mineralization of soybean residue and thus greater N input from soybean residues (Jones et al., 2016). Gupta et al. (2016b, 2017) have shown that higher baseflow in the Upper Midwestern United States is mainly due to increased precipitation in recent years and not due to land use changes (both increased tile drainage or adoption of soybeans in the cropping system) as suggested by Schilling and co-workers.

On a monthly basis, FWNC concentrations in all three rivers were higher early in the growing season (April, May, or June). These concentrations then decreased with time to a minimum value in August or September and then increase again near the end of the year. Higher FWNC concentrations earlier in the season reflect the unused nitrogen from the previous year as well as fall and spring applied nitrogenous fertilizer, higher soil wetness, and frequent rainstorms early in the season. Lower FWNC concentration in August and September reflect the lack of precipitation in these months, enough soil storage to capture rainstorms and high water and N use by crops and thus, less available N for tile drainage. The spread in FWNC concentrations was generally higher earlier or later in the season due to reduced water and N uptake as well as due to uncertainties in the timing of precipitation events. As in the case of Schilling and Lutz (2004), monthly FWNC concentrations were also related to the natural log of monthly baseflow but R^2 values of these relationships were lower in our study. This could be due to differences in the time period covered by two studies as well as other differences discussed earlier.

Regression analysis of monthly streamflow, baseflow, N-loads and FWNC concentration showed that Ln(streamflow), Ln(baseflow), and Ln(N-loads) were generally linearly related to precipitation in a given month and a few prior months. In some cases earlier in the season, these variables were also related to previous year's precipitation, an indication that some of the past water stored in the soil both above and below the drain tile is interacting with current months precipitation and affecting the streamflow and baseflow. In most cases, there was no effect of soybean area on monthly streamflow, baseflow, or N-loads. R^2 values for monthly regression relationships for these three variables were generally >0.5. Monthly FWNC was also linearly related to the monthly precipitation but only for one or two months. R^2 values of monthly FWNC regressions were generally lower than those of monthly streamflow, baseflow, and N-loads.

The N-fertilizer use on farms as well as from N atmospheric deposition in Iowa from 1987 to 2001 are plotted in Fig. 30. Although there is limited data on N addition from manure, it showed that N addition from both combined unconfined and confined sources in Iowa varied as 403,046; 324,711; 321,150; and 312,223 metric tons in 1982, 1987, 1992, and 1997, respectively. Overall, there is a very small change in N addition to land from year to year in Iowa. However, for each of the river analyzed in this study there was a large difference in N-loads between the years. For example, N-loads in the Raccoon River in 1988 and 1989 (two dry years) were 3,272 mt and 1,521 mt, respectively. Comparatively, the N-loads in 1992 and 1993 (two wet years) were 21,183 mt and 34,079 mt, respectively (Table 31). These higher N-loads in 1993 were in spite of the fact that N fertilizer addition in Iowa in 1993 was smaller (770,012 mt) than other years (for example 937,704 mt in 1994). Comparisons of the precipitation data for these years shows that higher losses in 1992 and 1993 were mainly due to higher precipitation and lower N losses in 1988 and 1989 were mainly due to lower precipitation. In other words, the current N-fertilizer input had a minimal impact on N-load in the river (Table 31). These comparisons distinctly suggest that N losses from these landscapes are controlled by the precipitation and not so much by N-fertilizer use. This raises the question whether N management practices can be manipulated enough in the current cropping systems to have a large decrease in N-loads in these rivers and in turn a major impact on the extent of the hypoxic zone in the Gulf of Mexico. These findings are consistent with the recent projections that climate change induced precipitation changes alone will increase riverine total N-loading by 19±14% in the United States by the end of the century under the "business-as-usual" scenario and this impact will be especially strong in Northeast and the corn belt of the United States (Sinha et al., 2017). This analysis thus suggests that under an increasingly wet climate of the recent period the only way to have a major impact on reductions in N-loads in rivers will be through a reduction in baseflow (tile flow) or some type of remediation technology that strips nitrate from tile water or a change in cropping systems. One of the ways to reduce tile flow could be through the use of surface inlets thus redirecting percolating water to overland flow. However, this practice will lead to an increase in sediment and sediment P in rivers. In terms of remediation technologies, there has been increased research in the use of bioreactors, saturated buffers, and wetlands. One of the limitations of these technologies is the lack of enough residence time early in the season when most nitrogen is lost. High residence time is needed early in the season due to the colder climate of the Upper Midwestern United States. To overcome the limitation of the above technologies is the use of commercial resin to strip nitrate from tile water by exchange processes. In this technology, the effect of temperature is rather small. The next chapter in this thesis deals with a feasibility study of using this resin technology to remediate nitrate from tile water in an agricultural landscape.

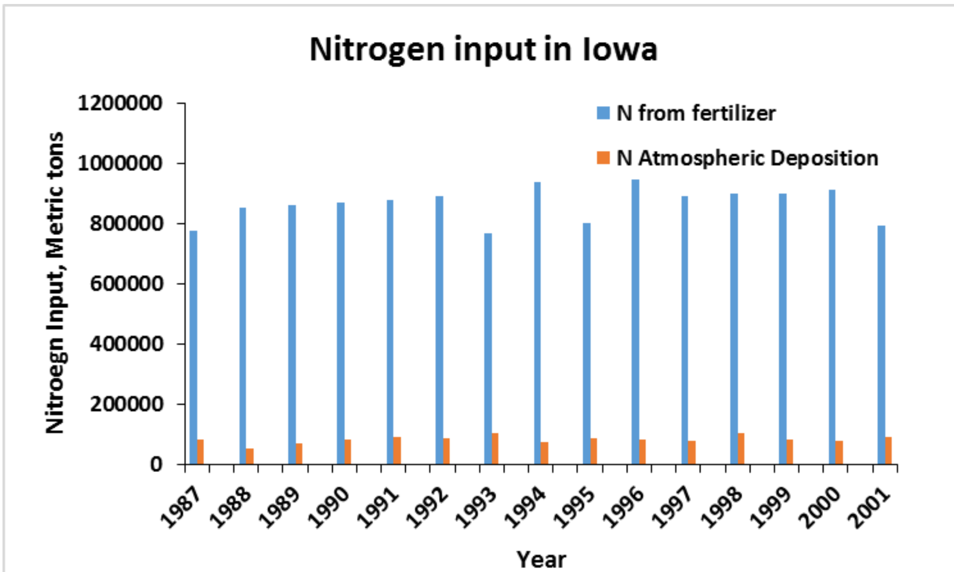

Figure 30: Comparison of nitrogen fertilizer used on farms and N atmospheric deposition in Iowa, 1987 to 2001 from Ruddy et al., 2006.

Table 31: Annual precipitation, fertilizer use, and nitrogen loads in the Des Moines River, Iowa River, and Raccoon River watersheds for dry years (1988-1990) and wet years (1991-1993).

	Des Moines River			Iowa River			Raccoon River		
Year	Ave. Annual Precip.	Fertilizer Use	N Load	Ave. Annual Precip.	Fertilizer Use	N Load	Ave. Annual Precip.	Fertilizer Use	N Load
	mm	mt/km^2	mt	mm	mt/km2	mt	mm	mt/km2	mt
1988	572	14747	4014	533	7396	15630	630	20477	3272
1989	546	15028	854	601	8116	4271	552	20927	1522
1990	881	15348	13716	1104	8154	97446	969	21433	16478
1991	1039	15660	61589	1037	8186	95579	1018	21929	32032
1992	864	16019	43042	899	8238	94630	889	22491	21183
1993	1207	14025	55685	1292	7160	174710	1097	19456	34080

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FEASIBILITY OF USING INDUSTRIAL ANION RESIN TO REMOVE NITRATE FROM TILE WATER

SYNOPSIS

Presence of nitrate in tile water is one of the major environmental challenges facing Midwestern agriculture. This project evaluated the feasibility of using industrial anion-exchange resins to remove nitrate from tile water. Resins are commonly used by urban and rural water works departments to strip nitrate from their water supply. The stripping process is similar to the household water softener and the resin can be repeatedly recharged with a solution containing chloride anions. The study involved a series of field and laboratory tests using two different resins, vertical and flatbed set-ups, and flow through and batch adsorption studies. This study was specifically undertaken with the premise to evaluate the use of potash as a regenerating agent such that resin captured NO_3-N can be recycled back to the land as KNO_3. This practice is different than the current practice of using NaCl as the regenerating agent and then dumping of $NaNO_3$ waste back into the river. The 2015 vertical column field-testing with 11-liters of resin from two different vendors showed that resin #1 retained 46% and resin #2 retained 26% of the nitrate in tile water from a soybean field. Subsequent field-testing of resin #1 in 2016 with tile water from two corn fields where hog manure had been applied showed the efficiency of resin varied from 7 to 34%. Since 2015 columns were used in 2016 testing, final cleanup of the columns at the end of the study period showed that this decrease in the efficiency was likely due to the presence or build-up of sulfate, organic anions and possibly bicarbonate ions on the resin over the two-year study period. Since the flow of tile water through the vertical resin columns was slow, we also tested the feasibility of using a flat-bed resin set-up that rapidly captured the tile NO_3-N and also could be easily and rapidly recharged in-situ. The results showed that the flatbed resin set-up reduced the NO_3-N concentration of tile water from 25 mg L^{-1} to a steady 16 mg L^{-1} rapidly. The higher leachate concentration in flat-bed set-up possibly reflects some bypassing of the tile water from interaction with resin as well as some interference from SO_4^{2-} and organic ions. Laboratory leaching studies with simultaneous leaching of NO_3^- and SO_4^{2-} showed affinity of the resin for both these anions, thus validating our interpretation of field results on decreasing efficiency of the resin over time to capture NO_3^- from tile water. Batch adsorption studies showed resin followed the Langmuir adsorption isotherm with maximum NO_3-N retention capacity of 156 mg g^{-1} of the resin. Both field and laboratory studies showed that there are some challenges in the use of industrial anion-exchange resin to remediate tile water at individual farm fields. These include the presence of sediment in tile water from cracked tiles and thus fouling up of the resin. Although we used the downward percolation of tile water through the resin column, air blockage likely slowed down the percolation of the tile water. Thus, a vertical upward feed of the tile water through the resin column will likely remove this problem but a system will need to be developed that will prevent blowout of the resin during high flow conditions. Presence of sulfate, bicarbonates, and organic anions in tile water will foul up the resin and reduce its efficiency. However, this problem can be overcome through more frequent cleaning of the resin as well as in developing better recharging techniques. Flatbed set-up can also be up-scaled to possibly boxes of 1 m^3 of the resin but that means setting-up larger recharging and cleaning containers in the field and supplying these containers more frequently with clean water. The field data also showed some concerns about batch adsorption of NO_3^- from water used for cleaning flatbed containers. Considering the large quantity of tile water that flows through main tiles in agricultural landscape of the Upper Midwest, we concluded that setting up of a common facility like that of water works will be a better mechanism than individual field set-ups like the one tested in this study. However, setting up and running of the common facility will be expensive. The results of this study do point out the potential use of this resin in remediating water in individual homes in the rural areas where groundwater may be high in NO_3 concentrations.

INTRODUCTION

Nitrate (NO_3^-) losses in tile-drained water from agricultural lands are one of the major environmental challenges facing Midwestern agriculture. Much of this NO_3^- is finding its way to the Gulf of Mexico and leading to the development of the dead or hypoxic zone (<2 mg L^{-1} dissolved oxygen). Depending upon the weather conditions in the Midwest United States, mid-summer hypoxic zone in the Gulf has varied from less than 500 km^2 in 1988 to as high as 22,720 km^2 in 2017 (NOAA, 2017), with long-term average corresponding to 14,000 km^2 (EPA, 2015). As a result of the hypoxia problem in the Gulf of Mexico, excess nitrogen (N) in Midwestern rivers is under heavy scrutiny. Two major reasons for excess N in the Gulf of Mexico are (1) the installation of subsurface drain tiles in agricultural fields of the Midwestern United States, and (2) the use of N-based fertilizers in these said fields (Alexander and Smith, 1990; Lucey and Goolsby, 1993; Rabalais et al., 1998; Goolsby et al., 1999 and 2001; and Petrolia et al., 2006). Although there are no good records on the length of drain tile installed in any of the mid-western states, it is generally accepted that there has been a steady increase in drain tile installation since the mid-1970's. This is mainly because of a wetter climate starting in the early 1970s as well as the easy and inexpensive nature of installing plastic drain tile. Plastic tile started being manufactured in 1967 in the United States (Fouss, 1974). However, initially, there was some reluctance in its adoption due to concerns that it may not withstand the freezing pressure of the soil in winter. Since the mid-1970s, plastic drain tile has been adopted for both the drainage of new lands as well as replacement of older clay and cement tiles that have degraded or have filled up with sediments (Gupta et al., 2011).

The upper Midwestern United States is a highly productive agricultural region of the world. However, a majority of the soils in this region are poorly drained (Gast et al. 1978). This is mainly because of the presence of impeding layers starting around the root zone depth. These impeding layers formed due to the massive overburden of glaciers during the past several glaciations. The soils in the region are also high in clay content (~30%) resulting in their lower permeability, thus leading to the development of perched water table conditions after snowmelt and spring rains (Baker et al., 1975; Gast et al., 1978; Kanwar et al., 1983, 1988; Buhler et al., 1993). These shallow water tables not only affect the development of plant roots in the soil but also hinder timely operations of field activities such as manure and fertilizer spreading, tillage, seeding, herbicide spraying, and harvesting with heavy machinery. The reason for installing drain tiles in these landscapes is to facilitate field operations in a timely manner as well as to provide an aerated root zone for profitable crop production. However, the negative effect of tile drainage is the leaching of soluble salts such as nitrate from the soil to ditches and streams and then to the Gulf of Mexico.

Nitrate in drainage water

There are two major sources of N in soils contributing to NO_3^- contamination of surface and ground waters: the soil organic matter and the land applied N-fertilizer or manure. A minor source of N in the Midwestern United States is N from atmospheric deposition (Ruddy et al., 2006). Most often N amendments in the Upper Midwestern United States are fall applied on land because of the constraints of wet soils in early spring. Nitrate leaching to drain tile occurs because NO_3^- is a soluble anion and it is carried downward with the percolating water. Much of the NO_3^- losses occur in early spring because of recharged soil profile from previous fall precipitation as well as wet soil conditions from snowmelt and early spring rains. Nitrate in the tile water includes not only the residual soil NO_3^- after fall harvest, but also the NO_3^- from mineralized organic matter and the fall- or spring-applied N amendments.

Efforts have been ongoing to understand and define the correct amount and timing of N application and thus minimize N losses from agricultural lands (Gast et al., 1978; Logan et al., 1980; Baker and Johnson, 1981; Bergström and Brink, 1986; Kanwar et al., 1988; Randall and Iragavarapu, 1995; Randall et al., 1997; Randall et al., 2003; Randall and Vetsch, 2005). However, these efforts have not been very successful in reducing N-loads in rivers. In Sweden, Bergström and Brink (1986) suggested that N leaching commonly occurs (1) in periods of high precipitation when the fields are not covered by crops, and (2) when there is over fertilization either accidentally or intentionally. These authors also found that an application of N-fertilizer greater than 100 N kg ha^{-1} to grain crops significantly increased the risk of damage to both ground and surface waters. Their study concluded that a balanced N-input with crop requirements was needed to limit high NO_3^- losses in drainage water. A modeling study by Randall and Mulla (2001) showed that N-fertilizer application at specific times in the spring can reduce N losses by 36% compared to a fall application of N-fertilizer. However, a six-year field study at Waseca, MN also showed that fall applications of N-fertilizer (urea) with or without a nitrification inhibitor have similar NO_3^- losses as spring application of N-fertilizer with or with a nitrification inhibitor (Randall and Vetsch, 2005). On average, NO_3-N losses over 6 years were 1.25, 1.12, 1.08, and 1.17 kg ha^{-1} cm^{-1} of tile water from fall-applied urea, fall-applied urea with nitrapyrin, spring applied urea and spring applied urea with nitrapyrin, respectively.

Besides the efforts to develop optimum N application rates that minimize N losses by leaching, efforts have also been underway to study various remediation technologies that can strip NO_3^- from tile drain water before it empties into streams and rivers. Many of these technologies have different limitations and thus, a varied degree of success. Examples of NO_3^-remediation technologies are bioreactors, controlled drainage, wetlands, saturated buffers, and cover crops.

The principle underlying remediation by a bioreactor is denitrification of NO_3^- by anaerobic microbes (Hoover et al., 2016). Since microbes need a carbon source for energy and that is supplied by adding woodchips in the bioreactor. Laboratory and field studies with woodchip bioreactors have shown rates of NO_3^- reduction as high as 98% (David et al., 2015). However, a risk associated with bioreactors, as well as with all denitrification systems, is the risk of releasing nitrous oxide (N_2O) to the atmosphere (Groh et al., 2015). Nitrous oxide is a greenhouse gas that has a global warming effect over 300 times greater than that of CO_2 (David et al., 2015). Another limitation of the bioreactors is the need for a high residence time of drainage water to denitrify NO_3^- into N gas. For example, Roser (2016) tested the efficiency of woodchip bioreactors to remove NO_3^- at hydraulic residence times (HRT) of 1.5, 8, 12, and 24-hours under warm and cold temperatures. The results showed that although NO_3^- concentrations decreased for all treatments from the inlet concentration of 20 mg N L^{-1} (as KNO_3), the treatments that had the greatest impact was the HRT of 24-hr. The mean NO_3-N concentration at the outlet was 5.1 mg L^{-1} NO_3-N for HRT of 24-hr compared to 18.9 mg L^{-1} NO_3-N for HRT of 1.5-hr. Without the adequate residence time, stripping of NO_3^- from drainage water becomes less efficient (Christianson et al., 2012). Recent increases in precipitation due to climate change have also resulted in more water draining out of the soil profile, thus forcing a shorter residence time for tile drain water.

Controlled drainage, also known as drainage water management, is based on the principle of keeping the water in the soil and thus inducing in-situ denitrification losses (Frankenberger et al., 2006). In other words, this method deals with the management of water table so as to induce additional denitrification losses without affecting crop yield. The depth of the water table is managed with a control structure at the drainage outlet. The water level is continuously adjusted throughout the growing season depending on the crop growth stage. Controlled drainage has been shown to reduce the volume of drainage water as well as the amount of NO_3^- leaving the landscape by 25-40% (Dittrich, 2017). One of the pitfalls of controlled drainage is that it works only on level ground. This means one will need many controlled drainage structures even on a gently rolling field.

Use of wetlands is another potential method for removing NO_3^- from agricultural drainage. This again works on the principles of anaerobic denitrification of nitrate in tile water. However, there is limited documentation on its long-term success and like bioreactors, it may also lead to the emission of N_2O (Groh et al., 2015).

Recently, saturated buffers (also known as vegetative filter strips, riparian buffers, buffer strips, and simply buffers) have also been suggested as another best management practice to remediate drainage water for NO_3^-. Saturated buffers are vegetated areas at the edge of fields or animal facilities to limit sediment and nutrient losses in field runoff (Dallaha et al., 1989; Phillips, 1989). Relative to other mechanisms, buffer strips are inexpensive to maintain. Nitrate reduction in the buffers occurs from microbial immobilization, plant uptake, and denitrification. The ultimate reduction of NO_3^- occurs when the water table in the buffer strip saturates an organic layer of soil and induces denitrification (Hill, 1996). Buffers, however, are limited by field topography i.e. flat landscapes would not benefit due to the raising and lowering of the water table within the buffer because it will also raise the water table height in the adjoining cropped field (Jaynes and Isenhart, 2014).

Lastly, cover crops have also been suggested as another best management practice to minimize N losses from agricultural landscapes. The underlying principle in the use of cover crops is to provide additional time for plants to take up residual N from the soil. When established in the fall, cover crops can reduce NO_3^- leaching in the spring

(Russel and Hargrove, 1989). Randall and Mulla (2001) suggested that compared to other row crops, the establishment of cover crops will result in less NO_3-N leaching. However, the Mississippi River basin lacks the desired market for cover crops (Randall and Mulla, 2001). Furthermore, establishment and sufficient growth of cover crops are difficult in the cool climate of the upper Midwest. Also in some years, evapotranspiration losses by the cover crop can deplete soil available water for subsequent agricultural crops.

The goal of this research was to test the feasibility of using a NO_3^- stripping technology (industrial anion-exchange resin) to remove NO_3^- from tile water under field conditions. A benefit of this practice is that NO_3^- adsorption on exchange resin is an instantaneous process and thus it does not require much residence time. This technology is currently being used by the Des Moines, IA Water Works to strip NO_3^- from river water and by Hastings, MN Water Works to strip NO_3^- from groundwater. However, most of these facilities use NaCl as a recharging chemical for the regeneration of the resin which results in the waste generation of $NaNO_3$ that is dumped downstream thus resulting in no net change in downstream NO_3^- loads. A specific objective of this research was to test the feasibility of using potash (KCl) as a recharging agent that would result in the generation of KNO_3 waste which can be put back on land as N fertilizer.

Ion Exchange Resins

The ion exchange resins are a copolymer that includes a functional group (or a functional group is subsequently introduced into its matrix) that captures ions from the water stream. The resin matrix could be a styrene or acrylic type depending upon the polymerization technique. The resin used in this study was a styrene type which is generally made up of polymerized ethenylbenzene-diethenylbenzene (Harland, 1994).

Resin technology for remediation of NO_3^- from surface and ground waters is similar to the technology used in household water softeners. This technology has been used in urban areas where NO_3^- levels are high in source water. The process includes passing of high NO_3^- water through the resin column and stripping its NO_3^- contents via the ion exchange process. The solid phase (ion exchanger) is insoluble, therefore, when placed in the aqueous solution its fixed cations react with the opposite ions in the solution. For example, an anion exchange process will be:

$$\underset{\text{Solid}}{M^+A^-} + \underset{\text{Solution}}{B^-} \rightleftharpoons \underset{\text{Solid}}{M^+B^-} + \underset{\text{Solution}}{A^-}$$

where M^+ is the insoluble fixed cationic complement in the M^+A^- ion exchanger and B^- is the solution phase anions that exchanges with exchanger anion A^- (Harland, 1994).

The phenomena of ion exchange have been known since the 1850's (Thompson et al., 1850, Way et al., 1850) but its commercial potential was not realized until 1896 (Harm, F., German Patent 95, 447 (June 2, 1896)). It was around mid-1940's that ion exchange was successfully used to the degree that we see it today, i.e., the development of polystyrene resin and the production of deionized (DI) water (Nachod, et al., 1965). Polystyrene resin is a crosslinked copolymer bead which is also elastic and thus can expand when taking in a solvent (Helfferich, 1995). Figure 1 shows an example of the versatile resin matrix that allows the resin to expand. Ion exchange resins are stable in all common solvents, however, can deteriorate by oxidation or thermal hydrolysis. Strong-base anion-exchange resins (the resin used in this study) can deteriorate at temperatures above 60 °C (Helfferich, 1995).

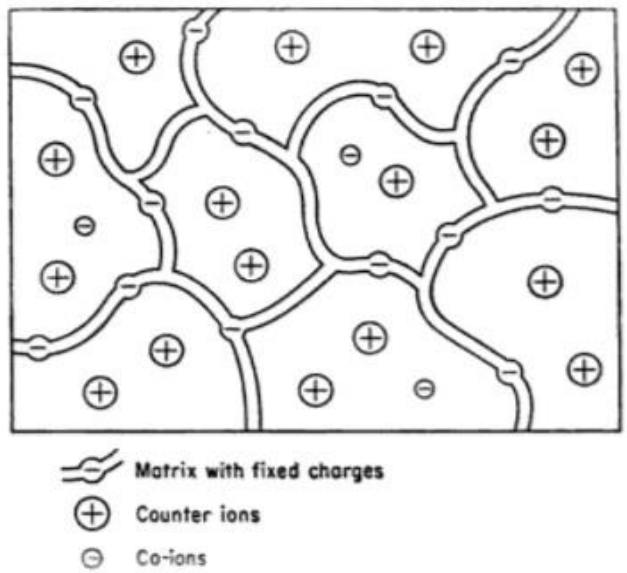

Figure 1: Schematic of ion exchange resin structure, a flexible, random network. Taken from Helfferich, 1995

There are numerous types of ion exchange resins with varying properties depending upon the composition, matrix crosslinking, and a number of fixed ionic groups. According to Harland (1994), ion exchange resin is one of the most cost-effective and easiest means to remediate NO_3^- from drinking water. For this study, the authors will focus on the use of a strong-base quaternary ammonium group anion exchange resin (TULSION A-32) that has a strong affinity for NO_3^-. The study will also evaluate the effectiveness of regenerating this resin with potash (KCl). The overall objective of this study was to evaluate the feasibility of using an anion exchange resin to remove nitrate from drain tile water under field conditions and to assess if KCl can be used as a recharging agent leading to the production of KNO_3 as a waste product that can recycled back to land as a fertilizer.

METHODS

A series of field and laboratory experiments were conducted to assess the feasibility of using anion resin for remediating NO_3^- from tile drain water in agricultural fields. The field experiments involved actual testing of the resin to remediate tile water under producers' field conditions. The laboratory experiments were designed to evaluate the anion resin's potential to adsorb NO_3^- and how this potential is compromised by presence of sulfate (SO_4^{2-}) and organic ions in tile water.

Field Studies

Field-testing of anion resin to capture NO_3^- from tile water was done in 2015 and 2016 at three farms near Vernon Center and Good Thunder in southern Minnesota (Figure 2). The basic set-up involved passing the tile water through a resin column and monitoring the flow rate and NO_3^- concentration at the inlet and outlet of the column.

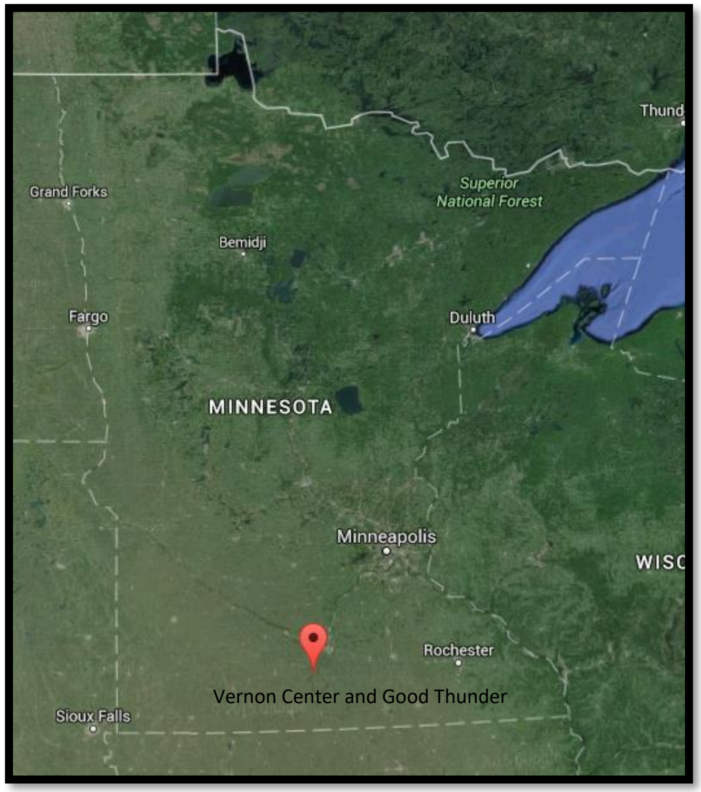

Figure 2: A map showing Vernon Center and Good Thunder, Minnesota where field experiments were conducted.

Resin columns consisted of Schedule 40 PVC pipe (15 cm ID x 76.2 cm long) with matching caps for the bottom. The caps were glued in place with a PVC primer and a cement. The caps had a 2.5 cm threaded hole in the center for attaching a 2.5 cm diameter valve that allowed percolating water to drain out of the column. The bottom inside of the cap was covered with a 15 cm diameter and 2.5 cm thick foam to prevent leakage of the resin from the column.

Each PVC column was filled with 11 liters of the resin by weighing the column before and after resin addition. The resin at the top of the column was then covered with a 15 cm diameter 2.5 cm thick foam followed by a perforated stainless steel plug to prevent resin from floating and spillage during infiltration of tile water into the PVC column. The plug was constructed by putting a stainless steel mesh between two PVC discs that were screwed together. The PVC discs were machined to create a groove on its side that kept a rubber O-ring in place. A metal handle was attached to the plug to ease its placement and removal from the PVC column. In two years of field study, there was some loss of resin from each column, due to washouts, broken filters, sediment cleaning, etc.

The first field-testing was done in 2015 at the edge of a fifty-acre soybean (*Glycine max*) field in Vernon Center, MN. To authors' knowledge, no fertilizer was applied to the field in 2015. The field had several 10 cm diameter subsurface plastic tiles buried around the rooting depth. However, there were no surface inlets in the field. During the study, we noticed some sediment in tile water right after rains thus indicating the presence of some cracks in drain tiles.

In the field, the PVC columns with resin were placed on a frame built from 4 fence posts held by 2 squares blocks made from 5cm x 10cm wood pieces (Figure 3). The frames allowed for easy replacement of the existing columns with recharged columns. A 10 cm diameter, 4.5 m long corrugated pipe without holes delivered the tile water from the field tile outlet to the resin columns. The open end of the corrugated pipe was then split into two lines with a "T" connector, each line emptying into an individual PVC column (Figure 3).

Figure 3: Field column set-up in 2015 study showing a corrugated plastic pipe supplying the tile water to two different resin columns placed on two fence post stands.

Starting May 2015, a small portion of tile water was allowed to infiltrate through each column. Since the tile flow rates were much higher than the column percolation capacity, excess tile water spilled out at the top of the column (Figure 4). Daily water samples were taken from both the drain tile as well as from the bottom of the column for NO_3^- analysis. We also measured the flow rate at the bottom of the column. We assumed that the water was flowing through the columns at a steady state rate. Water samples were brought back to a farmhouse where they were frozen and stored until picked up at the end of a week. These samples were then taken to the laboratory and again stored frozen until the time of the analysis. Each week the field columns were exchanged for clean, recharged columns and the used columns were taken back to the lab for recharging with a 13% KCl solution.

Figure 4: Tile outlet into a resin column. Since the flow of the water was higher than the percolation capacity of the resin column, there was some overflow of drain tile water.

Resin Recharging

Thirteen percent KCl solution was used to recharge resin columns brought back from the field. The solution was made by dissolving muriate of potash pellets (KCl) into DI water. Once dissolved at room temperature the solution was then filtered and stored in 15-liter carboys. Selection of 13% KCl solution for recharging resin columns was based on the estimated retentive capacity of 11-liter resin with its operating capacity of 520 meq L^{-1} (Charles Mahady of Tonka Water, personal communication). Together this resulted in a capacity of 355 grams of anion adsorption. These calculations assumed the negligible presence of SO_4^{2-} in drainage water. To cut down the generation of large quantities of wastewater, we also explored the idea of using higher concentration KCl solution. However, the use of higher concentration KCl solution for recharging resin columns has limitations. For example, KCl is only soluble to 25% (34.2 grams/100 ml of water) at 20 °C and 1 atm (Burgess, 1978). If we had used 25% KCl solution and if it had stayed longer in contact with the resin, there is a potential that it could have resulted in a batch condition leading to reverse equilibrium before all the NO_3^- is eluted off the resin. Furthermore, higher KCl concentrations could have also caused osmotic shock to the resin, reducing its lifespan. Since municipal systems use 10% NaCl as a recharging agent, this resulted in KCl equivalent of 13% solution. The higher volume of regenerate at low concentration results in more contact time for the KCl brine thus causing more NO_3^- to come off the resin.

The process of resin regeneration was a gravity fed (downward flow). It involved passing the KCl solution through the used column and collecting the leachate at the bottom (Figure 5). The KCl brine was run through the column at 1-bed volume (BV), followed with a rinse from DI water at 2 BV. Bed volume refers to the volume of the resin in the column, i.e., 1 BV is equal to 11 liters in this study. These recharge volumes and concentrations were recommended by the resin manufacturer. At one time during the resin regeneration and cleaning process, leachate along with tile water was also analyzed for heavy metals using the ICP-OES (Inductively Coupled Argon Plasma Optical Emission Spectrometer). This analysis was done mainly to assess if any harmful or unwanted chemicals were coming off the resin during regeneration.

Figures 5: Resin column leachate product after 13% KCl brine was passed through the column for recharge. One liter samples collected throughout the recharge process from first (far right) to last (far left). Brownish color in the leachate is an indication of dissolved organic matter captured by the resin from tile water.

In 2016, the field-testing was done at two locations in Good Thunder, MN. The first location (L1) was a tile outlet located just off a 16-hectare corn field (Figure 6a) whereas the second tile outlet (L2) was located in a ravine that ran from a 20-hectare corn field (Figure 6b). Unlike the field in 2015, the fields in 2016 had a thin coating of hog manure applied and incorporated previous fall. In a conversation with the farmer who manages these fields, both these fields have been annually sprayed with hog manure and then incorporated keeping the total N application within the recommended rates. The resin column set-up in 2016 was similar to the previous year, but only one column was placed at each site and only one type of resin was used (TULSION A-32).

a. 

b. 

Figures 6a-b: Resin columns set-up in 2016 for remediating drain tile water from hog manure applied fields at two locations (L 1 and L 2) in Good Thunder, MN

Final Cleaning up of the Resin Columns

After the field use of the resin columns for two growing seasons, a final cleanup of each column was conducted with a 2% NaOH and 10% NaCl solution. This step was undertaken in this study to assess the presence of SO_4^{2-} and organic compounds that may have interfered with retention of NO_3^- by the resin. This cleanup process was recommended by Tonka Water Works. During the clean-up process, a three-bed volume of 2% NaOH+10% NaCl solution was passed through the resin column followed by 3 BV of DI water for the rinse. The steps in the clean-up process included leaching of a single bed volume of 2% NaOH + 10% NaCl followed by the addition of a second bed volume of 2% NaOH + 10% NaCl solution that was held for 4 hours in the column and then allowed to drain. This was followed by the leaching of a third (final) bed volume of 2% NaOH+ 10% NaCl solution before rinsing the resin with DI water. All the leachate from the cleaning process was collected and then analyzed for NO_3^-, SO_4^{2-}, alkalinity, and total organic carbon contents.

Flatbed Resin Set-up

Since tile water percolation through the vertical resin column was slow and since the columns took a long time to recharge, we also tested the idea of using a flatbed resin set-up in the field both to increase the flow of tile water through the resin as well as to quickly recharge the resin in-situ. The flatbed resin set-up consisted of a rectangular plastic container (55 cm long x30 cm wide, and 11 cm high) that was perforated both at the bottom and on the sides (Figure 7). A fine mesh (MG size 40) stainless screen was screwed on to the bottom and the sides to prevent the outflow of resin from the box. The box was filled with 11 liters of resin and then sealed with fine and coarse mesh stainless screens in that sequence. A set of four Plexiglas plates were then mounted on the edge of the plastic box to extend its height by another 12 cm. This extended enclosure helped keep tile water above the screens long enough to percolate through the resin without overflowing.

The effectiveness of the flatbed set-up was tested by placing it at the end of an active tile outlet originating from a cornfield (Figure 7). The perforation at the bottom and on the side of the box allowed a radial discharge of the tile water out of the box. One of the main advantages of the flatbed was the idea of recharging onsite. After about a day in the field, the flatbed was recharged onsite with 13% potash (KCl) solution. The recharging process involved soaking the flatbed for five minutes in 132-liter plastic bins filled with 50 liters of 13% potash (KCl) solution. This step was followed by a series of three washes with the DI water, again by soaking the flatbed for five minutes in three 132 liter bins each containing 50 liters of DI water (Figure 7b-d). During recharge and wash cycles, the flatbed container was shaken in each bin to ensure good contact between the resins and the recharging solution or the wash water. After rinsing, the flatbed was returned to the tile outlet.

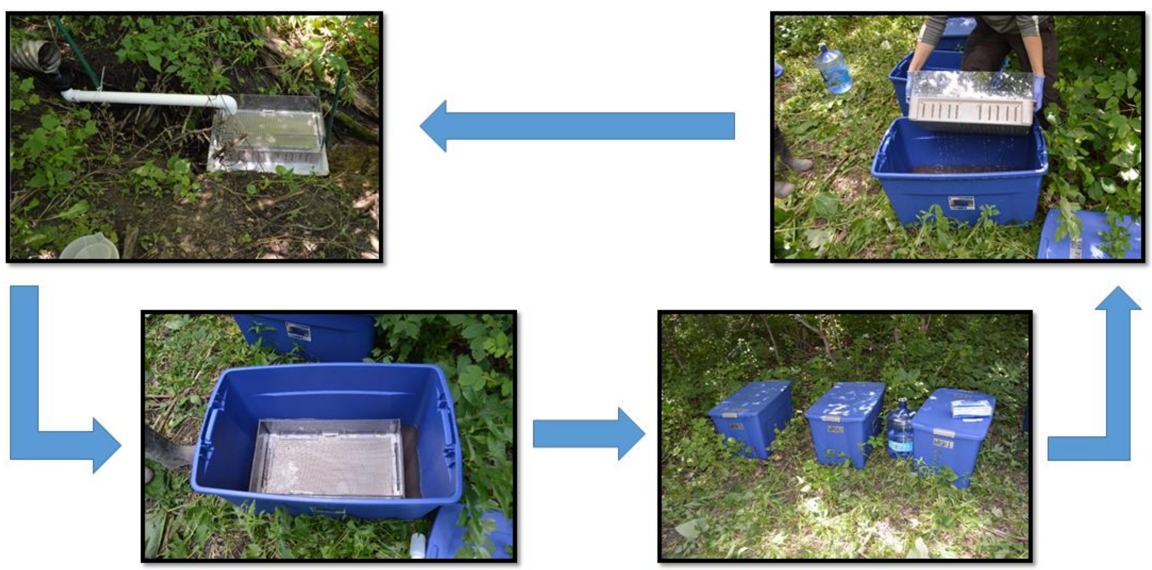

Figure 7: Pictures of a flatbed resin set-up in the field. The arrows indicate the steps in the recharge and wash process. Starting from the top left, the pictures show tile water entering the flatbed resin box and after one day the box is removed and placed in 13% KCl solution for 5 minutes (bottom left). After the soaking in KCl, the box is dipped and shaken into three separate wash stations (bottom right), lastly, the box is removed from the final wash station and replaced back under the tile outlet (top right).

Three separate procedures were run with the flatbed. Each of these procedures took place on different days. In the first procedure, the flatbed was placed under the tile outlet for 3.5 hours while 4 samples were taken from the water that flowed out of the flatbed. Samples were taken at the 0min, 30min, 1hr, and the 3.5hr increment. Similar to the first procedure, in the second attempt, the process was run for 3 hours and 2 minutes. Twelve samples were taken from the flatbed at the 0min, 5min, 10min, 20min, 40min, 70min, 100min, 160min, 162min, 167min, 172min and the 182min increments. In the third procedure, a set of samples were taken daily from 1 to 4 July 2016 for several days. The flatbed was also recharged onsite daily and placed back under the tile outlet. Right after its placement under the tile, another sample was taken from the flatbed to monitor changes to the resin after recharge. Samples were also taken from the recharge and wash stations to evaluate the amount of NO_3^- in each bin.

Laboratory Studies

The laboratory experiments involved (1) leaching studies through a series of small resin-filled columns to test the interference of SO_4^{2-} ions on potential retention of nitrate by the resin, and (2) batch adsorption tests to assess the maximum potential of resin to retain NO_3^-. Both tests were run with and without the presence of SO_4^{2-} ions. The resin used in the laboratory studies was TULSION A-32. In Table 1 are listed some of its characteristics. The particle size of the resin was approximately 0.3 to 1.2 mm and had a total exchange capacity of 1.3 meq L^{-1}.

Table 1: Typical Characteristics - TULSION® A-32

Type	Strong Base Anion Exchange Resin
Matrix	Polystyrene Copolymer
Functional group	Quaternary Ammonium Type II
Physical form	Moist spherical beads
Ionic form	Chloride
Total exchange capacity (minm.)	1.3 meq/ml
Swelling (approx.)	Cl^- to OH^- 12%
Moisture content	47 ± 3%
Maximum temperature stability	60° C (140° F)
Backwash settled density	43 to 45 lbs/ft^3 (630 to 720 g/l)
pH range	0-14
Solubility	Insoluble in all common solvent

Column Studies

Two sets of small column leaching studies were run to test the interference of SO_4^{2-} ions on NO_3 adsorption by the resin. The first set of columns were two high-density polyethylene cartridges (6.5 cm diameter, 25 cm long) that were fitted with ⅜ inch nylon barbs at the bottom to facilitate leachate collection during the breakthrough experiment (Figure 7). Before packing the cartridge with resin, a stainless steel screen was placed at the bottom of the cartridge to prevent resin from flowing out of the column during the breakthrough test. Each cartridge was then packed with 612 mL of anion exchange resin. This was an equivalent of a pore volume of 269 mL. At the top of each cartridge, a 0.5-inch foam barrier was placed to allow the solution to infiltrate into the resin but prevent the resin from floating out of the cartridge. Each cartridge was then eluted with different leaching solutions.

Figure 8: A set of two high-density polyethylene cartridges (6.5 cm diameter, 25 cm long) that were packed with 612 mL of anion exchange resin. Column number 1 (left) treated with sodium nitrate ($NaNO_3$) solution to assess the extent of nitrate retention by the resin. Column number 2 (right) treated with 50 mg L^{-1} sodium nitrate ($NaNO_3$) plus 10 mg L^{-1} potassium sulfate solution to assess the interference by SO_4^{2-} ions on NO_3^- adsorption by the resin. Column 2 shows the wetting front as it was being saturated from bottom up to expel the air.

The first leaching set-up involved the leaching of 7.5 bed volumes (BV) of 50 mg L^{-1} NO_3^- ($NaNO_3$) solution through the resin followed by 7.5 BV leaching of 10 mg L^{-1} SO_4^{2-} (K_2SO_4) solution. This experiment was conducted to assess the extent of nitrate retention by the resin and then evaluate the potential of SO_4^{2-} ions to displace adsorbed NO_3^- ions from the resin. The second leaching set-up involved the leaching 7.5 BV 50 mg L^{-1} NO_3^- plus 10 mg L^{-1} SO_4^{2-} solution through the resin. This experiment was conducted to assess SO_4^{2-} ion interference on NO_3^- adsorption by the resin during leaching.

Before the start of the leaching tests, the resin in both cartridges was saturated with DI water from the bottom up in order to expel the air out of the resin. Once fully saturated, each resin column was eluted under gravity with five liters of the treatment solution. The leachate samples were then collected at designated pore volumes and analyzed for NO_3^-, NO_2^-, Cl^-, Br^-, F^-, SO_4^{2-}, and PO_4^{3-} using ion chromatography. The difference in the amount of NO_3^- and SO_4^{2-} added in the percolating solutions to what leached out of the cartridges was the amount of NO_3^- and SO_4^{2-} retained by the resin.

Since the above leaching test showed that we were using too much resin relative to the amount of NO_3^- in the solution, two additional leaching tests were performed with smaller amounts of the resin. For this test, 0.5 mL of wet resin was packed in a 3 mL syringe and then eluted with 1000 mL of 100 mg L^{-1} NO_3^- ($NaNO_3$) solution (Figure 9). Again, before packing the resin in the syringe, a stainless steel fine mesh was placed at the bottom of the syringe to prevent resin leaching out of the column.

Figure 9: Plastic 3 mL syringe packed with 0.5 mL of saturated resin.

Batch Adsorption Studies

The batch adsorption test involved testing the potential of TULSION A-32 resin to adsorb NO_3^- and SO_4^{2-} at various solution concentrations. In this test, 2 g of the resin was mixed with 50 mL of (1) $NaNO_3$ solution or (2) K_2SO_4 solution at various concentrations in centrifuge tubes. The NO_3^- and SO_4^{2-} concentrations used in the batch mode were 0, 5, 10, 25, 50, and 100 mg L^{-1}. Adsorption at each concentration was replicated twice for a total of twelve samples per solution (24 samples total). Resin and the solution were then mixed on a rotary mixer at room temperature for one hour. After mixing, the suspensions were filtered through the Whatman filter paper #50 and the filtrate analyzed for NO_3^-+ NO_2-N, SO_4-S, and various halides using ion chromatography.

The second batch study was run similar to the first batch study except for 0.05 g of the resin was mixed with 50 mL of $NaNO_3$ solution at various concentrations. The NO_3^- concentrations in this batch study were: 0, 5, 20, 40, 60, 80, 100, 150, and 200 mg NO_3^- L^{-1}. Again, the resin and the solution were mixed in a rotating mixer at room temperature for 24 hours. After mixing, the supernatant solution was poured out for NO_3^-+ NO_2-N, SO_4^{2}-S, and various halides analysis using the ion chromatography.

The adsorption isotherm of the resin was developed by fitting the Langmuir Equation (Eq. 1) to the batch data on NO_3^- retained by the resin vs. NO_3^- in the equilibrium solution. The best fit was obtained by linearizing Eq. (1) and estimating the values of S_{max} and $K_{L.}$ The reason for using the Langmuir equation was because it is primarily used for monolayer sorption, i.e., all the molecules interact with the surface layer, for a surface that has a finite number of sorption sites.

$$q = \frac{S_{max} \times K_L \times C_e}{(1 + K_L \times C_e)} \qquad Eq. 1$$

where q is the amount of NO_3^- adsorbed per unit weight of resin at equilibrium (mg g^{-1}), C_e is the equilibrium concentration of NO_3^- (mg L^{-1}) in solution, S_{max} is the maximum sorption of this resin for NO_3^- (mg L^{-1}), and K_L is the constant related to binding strength of the resin.

All chemical analysis in this research study was done by the University of Minnesota Research Analytical Laboratory (http://ral.cfans.umn.edu/tests-analysis/water-analysis).

RESULTS

2015 Field Study

In 2015, tile water passed through the resin columns for a total of 50 days for resin #1 and 48 days for resin #2. Figures 10 and 11 show the variation in NO_3-N concentration over time in tile water as well as in the leachate that came out of the resin column. Times, when the NO_3-N concentration in the leachate (blue line) was equal or greater than the concentration in tile water, indicated the resin has reached its exchange capacity. Those were also the times when columns in the field were replaced with recharged resin columns. NO_3-N concentration in tile water generally corresponded to about 15 mg L^{-1} during the study period. Comparatively, NO_3-N concentrations coming from the resin were around 2-3 mg L^{-1} right after recharged columns were installed. During the test period of 50 days, a total of 664 g of NO_3-N passed through resin column #1 and 313 g was retained (Table 2). Comparatively, 1,031 g of NO_3-N passed through the resin column #2 over 48 days and 271 g of nitrate was retained by the resin (Table 2). This corresponded to NO_3-N retention efficiency of 46% for resin #1 and 26% for resin #2. The difference in the amount of NO_3-N passing through different resin columns is likely due to differences in flow rate between the resins. Some of these differences in flow rate could be due to air blockage in columns during vertical low.

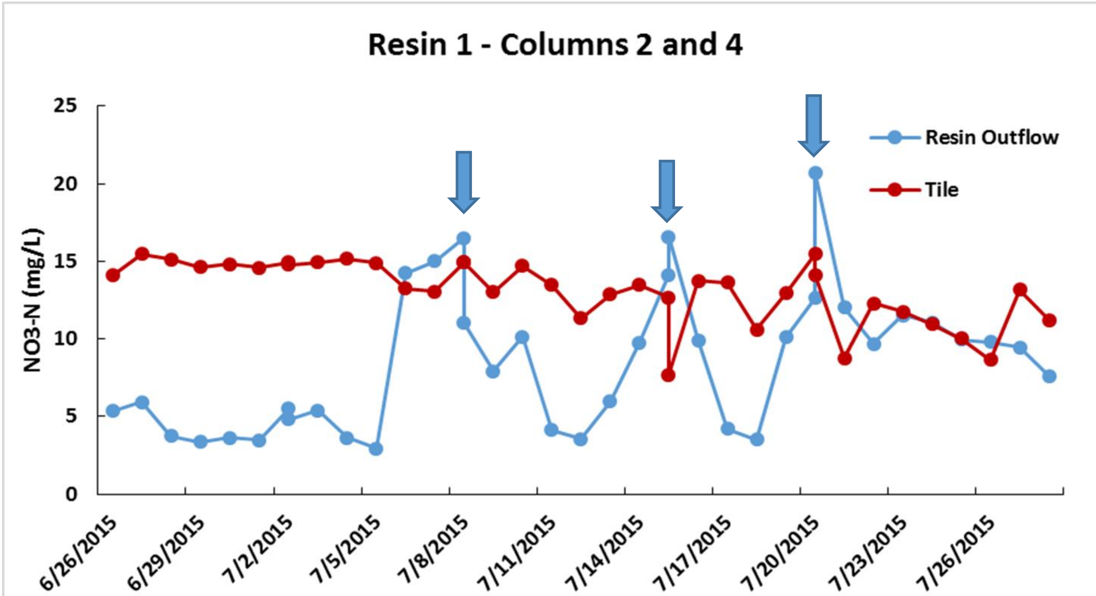

Figure 10: Plots of NO_3-N concentrations in tile water and leachate coming out of columns 2 and 4 representing resin #1 over the 50 day study period in 2015. Arrows show when the field column was replaced with a recharged column.

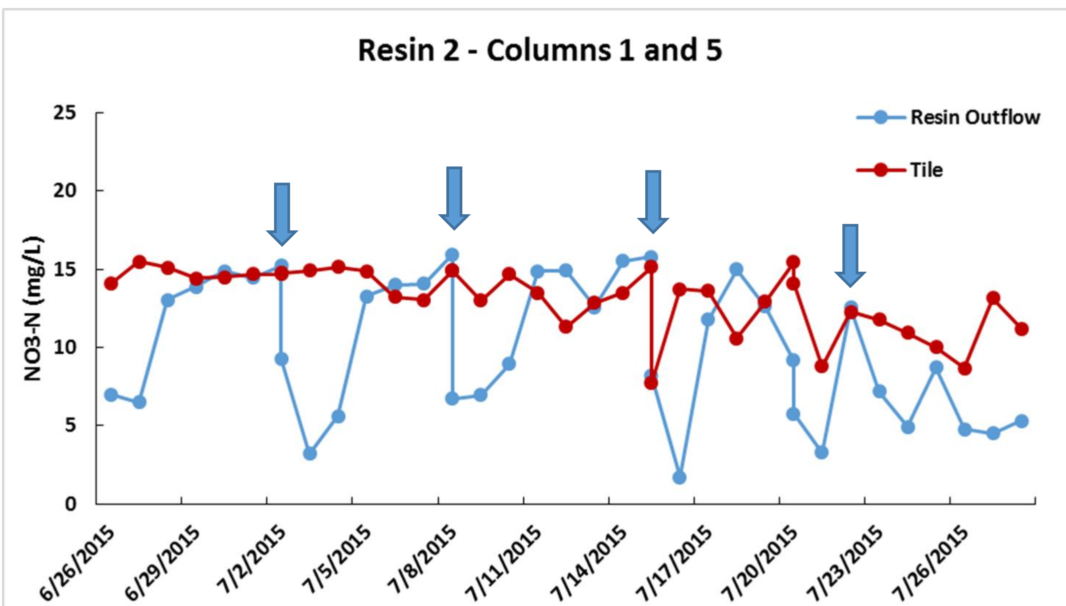

Figure 11: Plots of NO_3-N concentrations in tile water and leachate coming out of columns 1 and 5 representing resin #2 over the 48 day study period in 2015. Arrows show when the field column was replaced with a recharged column.

Table 2: A summary of total nitrate passing through and retained by two different resins under field conditions in 2015.

RESIN TYPE 1						
Date In	**Date Out**	**Days Total**	**Column #**	**NO_3-N In (g)**	**NO_3-N Out (g)**	**Net Retained NO_3-N(g)**
5/19/2015	5/30/2015	11	2	123	67	56
6/2/2015	6/9/2015	7	4	188	102	86
6/26/2015	7/2/2015	6	2	45	20	25
7/2/2015	7/8/2015	6	4	102	40	62
7/8/2015	7/15/2015	7	2	87	55	32
7/15/2015	7/20/2015	5	4	74	34	40
7/20/2015	7/28/2015	8	2	50	37	13
Total		50		668	355	313

RESIN TYPE 2						
Date In	**Date Out**	**Days Total**	**Column #**	**NO_3-N In (g)**	**NO_3-N Out (g)**	**Net Retained NO_3-N(g)**
5/19/2015	5/28/2015	9	1	177	95	81
6/2/2015	6/9/2015	7	5	184	136	49
6/26/2015	7/2/2015	6	5	163	129	34
7/2/2015	7/8/2015	6	1	111	85	26
7/8/2015	7/15/2015	7	5	189	166	23
7/15/2015	7/20/2015	5	1	120	100	19
7/20/2015	7/28/2015	8	5	88	49	39
Total		48		1031	760	271

2016 Field Study

In 2016, there were two monitoring fields. However, only resin #1 was used at both sites primarily because resin #1 was more efficient in retaining NO_3-N than resin #2. Tile water was passed through the columns for a total of 55 days at location 1 (Figure 12) and 31 days at location 2 (Figure 13). NO_3-N leaching behavior of resin was similar to that observed in 2015. On average, NO_3-N concentration in tile water varied around 45 mg L^{-1} at location #1 compared to around 30 mg L^{-1} at location #2. The higher NO_3-N concentration at these locations relative to 2015 location was likely due to continued hog manure application at these sites. At location #1, the NO_3-N concentrations in tile water were generally lower (35.4 mg L^{-1}) early in the season (7 April-25 May) and then slightly increased (41.0 mg L^{-1}) but remained relatively stable for rest of the study period. Early season lower NO_3-N values at location #1 are likely an indication of cooler temperatures and less mineralization of soil and manure organic N. Since monitoring started late at location #2, NO_3-N concentrations were relatively constant over the monitoring period.

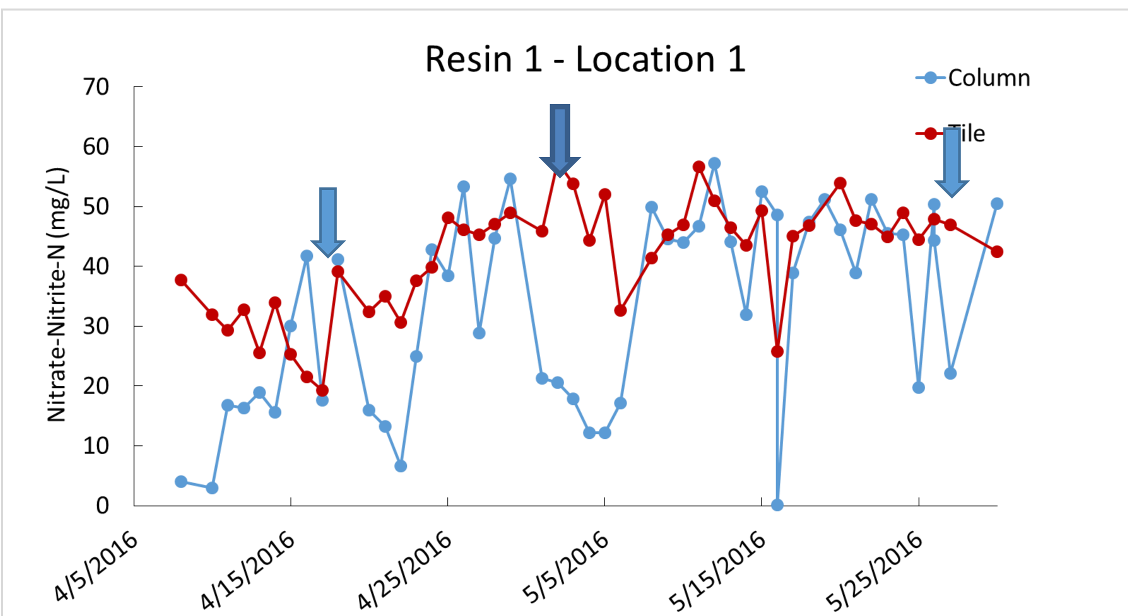

Figure 12: Plots of NO_3-N concentrations in tile water and leachate coming out of resin columns at location #1 in 2016. Arrows show when the field column was replaced with the recharged column.

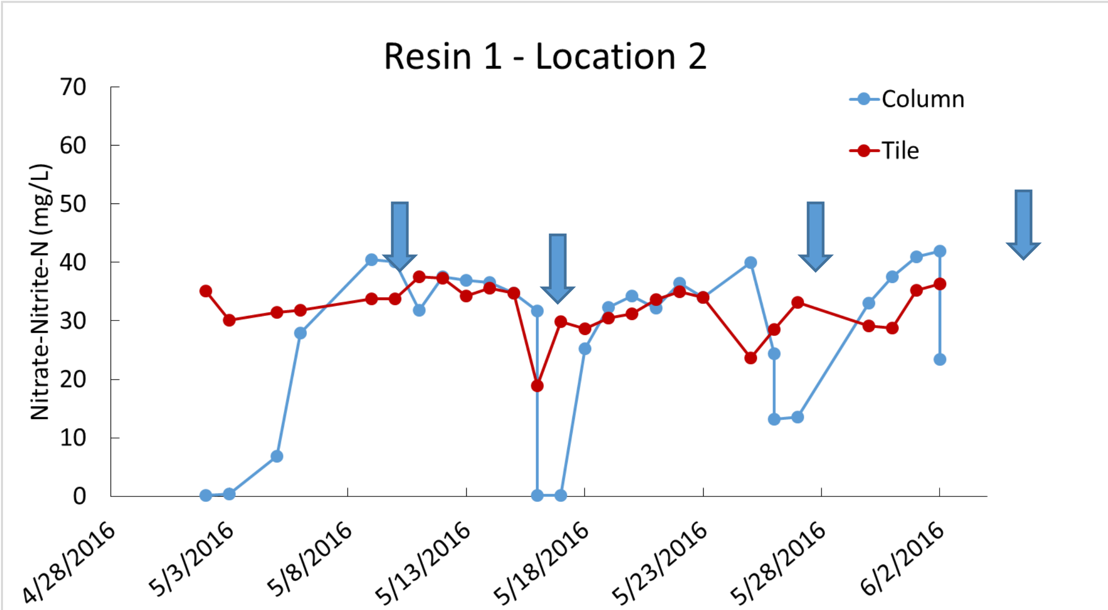

Figure 13: Plots of NO_3-N concentrations in tile water and leachate coming out of resin columns at location #2 in 2016. Arrows show when the field column was replaced with the recharged column.

The NO_3-N retention behavior of resin #1 at these two locations was similar to what was observed in 2015 i.e. right after the installation of the recharged column, nitrate leaching from columns was lower but after a few days, the NO_3-N concentration was similar to or higher than those of tile water. The higher NO_3-N concentration in the leachate relative to tile water indicated resin was reaching its retention capacity. A seasonal total of 1718 g passed through the columns at location 1 (L1) out of which 593 g was retained by the resin. Similarly, 656 g of NO_3-N was passed through the resin columns at location 2 (L2) out of which 48 g was held by the resin (Table 3). These differences in retention of NO_3 between the sites could be that columns used at site 2 were not fully cleaned and thus there were less adsorption sites available for subsequent NO_3 adsorption.

When using strongly basic anion exchange resins for NO_3^- removal, Harland (1994) showed that initially nitrate and other anions in water are reduced very effectively resulting in discharge water that is very high in chloride concentration. Later in the exchange cycle, HCO_3 starts replacing the residual chloride on the exchange resin while still retaining NO_3^- and SO_4^{2-}. However, near the end of the exchange cycle, sulfate starts displacing NO_3^- on the exchange resin thus increasing NO_3^- concentration in the discharge water. Since our tile water contained some levels of SO_4^{2-} (Table 4), this process explains why the concentrations of NO_3-N in our field studies exceeded that of the tile water just before the columns were taken down for recharging (Figs. 10-13). The displacement of adsorbed NO_3^- from the resin column is also supported by the presence of high levels of sulfur in the leachate during weekly resin recharge (Table 4). Substantial presence of total organic carbon and SO_4^{2-} in the leachate during the final cleaning of resin columns with NaOH+NaCl cleaning solution (Table 5) further supports Harland (1994) observation that NO_3^- in our resin columns was in competition with other ions like SO_4^{2-} for the adsorption sites.

Table 3: A summary of total nitrate passing through and retained by resin #1 at two locations in 2016.

Location	Duration (days)	Total NO_3-N Passed Through Columns (g)	Total NO_3-N in Tile Water (g)	Total NO_3-N Adsorbed (g)	Efficiency (%)
1	55	1125	1718	593	34.5
2	31	608	656	48	7.3

Chemical Analysis of Recharging Leachate

The concentration of various heavy metals and other cations in the leachate resulting from recharging of the columns are listed in Table 4. In general, the heavy metal and cation concentrations were less than the limit of the instrument. However, there were a few exceptions like K, Ca, Mg. and S. Potassium concentrations in the recharging leachate were higher because we used KCl as a recharging agent. Levels of K averaged at 627 mg L^{-1} coming from the columns whereas tile water concentration was 33.2 mg L^{-1}. Ca and Mg concentrations are also slightly higher than the corresponding tile water concentrations. It is possible that some Ca and Mg may have been present in natural potash. Sulfur concentrations averaged around 75 mg L^{-1}, a relatively high concentration compared to S concentration in tile water (1.3 mg L^{-1}) (Table 4). These high S concentrations in the recharging leachate would suggest a significant retention of sulfate ions from tile water and thus possibly (1) lowering the efficiency of the resin to retain NO_3-N from tile water, and (2) expulsion of adsorbed NO_3-N on the resin thus resulting in higher NO_3-N concentration in field leachate relative to tile water (Figures: 10 to 13).

Table 4: ICP analysis of the leachate samples after recharging resin columns with KCl solution and the tile water, All values are in ppm.

Sample ID	Al	As	B	Ba	Be	Ca	Cd	Co	Cr	Cu	Fe	K
1	< 0.08	< 0.01	0.15	0.18	< 0.01	16.8	0.02	< 0.01	< 0.01	0.15	< 0.02	624.4
2	< 0.08	< 0.01	0.12	0.19	< 0.01	18.18	< 0.01	< 0.01	< 0.01	0.16	< 0.02	685.2
3	< 0.08	< 0.01	0.22	0.81	< 0.01	15.27	< 0.01	< 0.01	< 0.01	0.2	0.02	698.2
4	< 0.08	< 0.01	0.13	0.28	< 0.01	9.47	0.03	< 0.01	< 0.01	0.59	0.03	644.6
5	< 0.08	< 0.01	0.12	0.07	< 0.01	5	0.03	< 0.01	< 0.01	0.16	< 0.02	488.8
Tile	< 0.08	< 0.01	0.01	0.05	< 0.01	14.29	< 0.01	< 0.01	< 0.01	0.02	< 0.02	33.2

Sample ID	Li	Mg	Mn	Mo	Ni	P	Pb	Rb	S	Sb	Se	Si
1	0.02	21.19	< 0.01	0.24	< 0.02	0.58	< 0.18	< 0.08	18.44	< 0.01	0.07	0.09
2	0.03	25.15	< 0.01	0.19	< 0.02	0.57	< 0.18	< 0.08	14.02	< 0.01	0.08	0.11
3	0.04	27.57	< 0.01	0.62	0.03	1.86	< 0.18	< 0.08	212.6	< 0.01	1.05	0.72
4	0.04	22.22	< 0.01	0.38	< 0.02	0.71	< 0.18	< 0.08	79.59	0.08	0.33	0.35
5	0.11	12.48	< 0.01	0.14	< 0.02	0.38	< 0.18	< 0.08	53.43	0.02	0.16	0.17
Tile	0.01	10.4	< 0.01	< 0.01	< 0.02	< 0.37	< 0.18	< 0.08	1.13	0.02	< 0.01	0.15

Sample ID	Sr	Ti	Tl	V	Zn
1	< 0.01	< 0.01	< 0.01	< 0.01	0.1
2	< 0.01	< 0.01	< 0.01	< 0.01	0.06
3	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
4	< 0.01	< 0.01	< 0.01	< 0.01	0.27
5	< 0.01	< 0.01	< 0.01	< 0.01	0.51
Tile	< 0.01	< 0.01	< 0.01	< 0.01	0.04

Final Clean-up Analysis

Table 5 lists the amount of NO_3-N, SO_4-S, alkalinity, and total organic carbon that leached out of various resin columns. As expected, there was some NO_3^--N present on the resin after the completion of field studies. However, there were also high amounts of SO_4-S and carbon in various columns. For example, SO_4-S concentrations ranged from 4 to 212 g in column 3-5. Comparatively, total organic carbon ranged from 23 to 61 g. Except for column#1, alkalinity for the other three columns was less than 2 mg $CaCO_3$/L.

In column #1, the alkalinity levels are very high (1248 mg $CaCO_3$/L) but the reasons for this anomaly between columns is not apparent.

Presence of both SO_4^{2-} and total organic carbon supports our earlier observation that there was some interference of NO_3^- adsorption by the presence of SO_4^{2-} and organic anions in the tile water. Although we did not use different columns between 2015 and 2016 field tests, it is likely that some buildup of SO_4^{2-} occurred over time in these columns and as a result, there was a reduction in NO_3^- retention efficiency in 2016 relative to 2015.

Table 5. Nitrate-N, sulfate-S, total organic carbon, and alkalinity from 2% NaOH + 10% NaCl wash of columns.

Column ID	NO_3-N (g)	SO_4-S (g)	Total Organic Carbon (g)	Alkalinity (mg $CaCO_3$ L^{-1})
2	21	4	23	1247.8
3	25	212	59	<2
4	47	52	61	<2
5	52	111	57	<2

Flatbed Set-up

The flatbed set-up was tested on three separate occasions. The first testing occurred on June 11^{th,} 2016. A plot of NO_3-N concentration in tile water and the resin leachate as a function of time is shown in Figure 14. Within the first hour, the resin reduced NO_3-N concentrations in the tile water from 27 mg L^{-1} to 5 mg L^{-1} again suggesting an instantaneous adsorption process. The presence of some NO_3-N in the resin leachate (5 mg L^{-1}) is likely from by-passing of some tile water along the edges of the flatbed box. In this test, the total time for resin in the flatbed to reach its capacity was 3 hours and 36 minutes. In this test, the flatbed set-up retained 37% of the NO_3-N from tile water. However, the resin capacity was met in just one day of flatbed operation compared to a typical vertical resin column set-up that lasted a week. The flatbed results are encouraging in that the set-up can be scaled up to a 1 m cube box filled with resin and that set-up will likely last several hours to a day depending upon the concentration of NO_3-N in tile water and the degree of tile water and resin interactions.

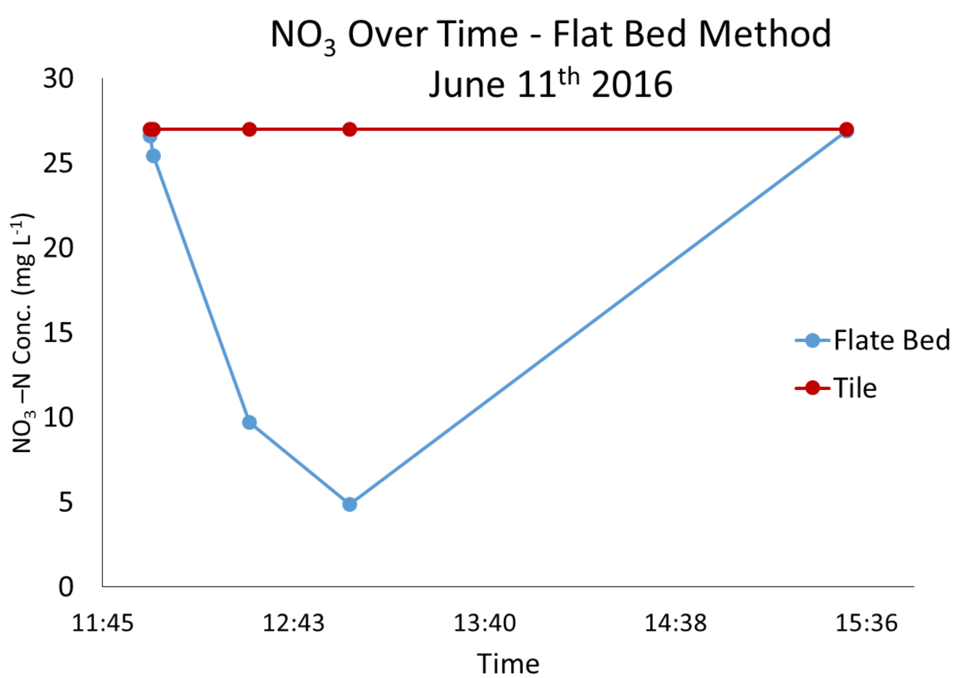

Figure 14: NO_3-N concentrations in tile water and the leachate from the resin in a flatbed set-up on June 11th, 2016.

A second test of the flatbed was performed at the same site on June 23rd, 2016. The resin reduced the NO_3-N concentration of the tile water from 25 mg L^{-1} to a steady average of 15.6 mg L^{-1} over a period of 3 hours. Higher NO_3-N concentration in the leachate in this test relative to the first test was likely from some by-passing of the tile water (without resin interaction) from the side of the box and possibly due to incomplete recharge of the resin resulting from SO_4^{2-} and organic anions occupying the resin exchange sites.

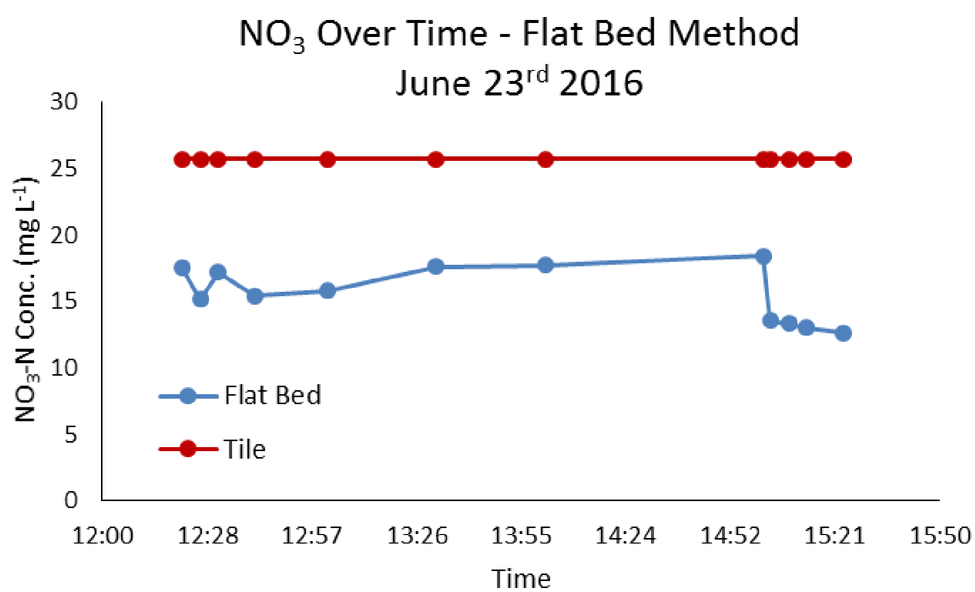

Figure 15: Plots of NO_3-N concentrations in tile water and the leachate from the resin in a flatbed set-up on June 23rd, 2016.

In a third test of the flatbed, samples were taken for a consecutive four days starting on July 1st and ending on July 4th, 2016. Results showed once again, NO_3-N being retained by the resin from the tile water (Figure 16). Noticeably, on the first day of the test, the flatbed was 3.2 mg L^{-1} higher than the tile water, but in the following three days it was continuously lower at an average of 4.0 mg L^{-1} NO_3-N. Data on the analysis from the bin water is given in Table 1.D. Samples from the onsite recharging station showed high concentrations of NO_3-N in the recharge bin (ranging from 6,323 to 17,793 mg L^{-1} NO_3-N), and all three wash stations (ranging from 28 to 4,573 mg L^{-1} NO_3-N). The decrease in recharge bin concentration over time suggests that the resin was adsorbing up some NO_3-N as it was dipped in the recharging solution (i.e. there was some batch adsorption occurring during recharging and thus this may not be the best way to recharge the resin boxes). Vertical leaching where nitrate is removed in the leachate will be the preferred method for recharging of these resin columns.

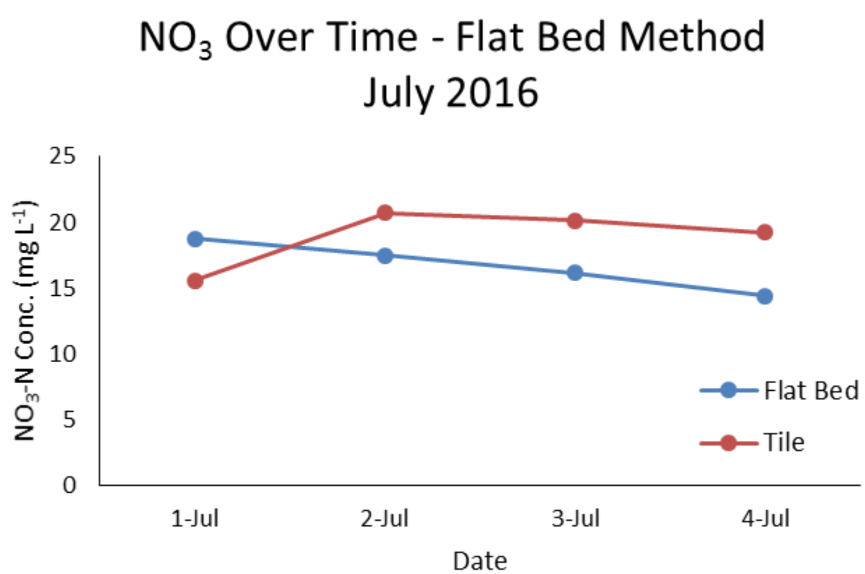

Figure 16: Plots of NO_3-N concentrations in tile water and the leachate from the resin in a flatbed set-up from July 1st to July 4th, 2016.

Laboratory Studies

Leaching Tests

The first set of laboratory studies involved leaching of NO_3^- ($NaNO_3$) and SO_4^{2-} (K_2SO_4) solutions through 6.5 cm diameter and 25 cm long polyethylene cartridges. In this study, the first test was leaching of 50 mg L^{-1} NO_3 solution through a resin column followed by leaching with 10 mg L^{-1} SO_4 solution. This test was designed to assess if there is any displacement of resin adsorbed NO_3^- by SO_4^{2-} ions. In Figures 17 and 18 are respectively plotted the relative concentration of NO_3^--N and SO_4^{2-}-S in the leachate as a function of bed volume. For both anions, the concentration in the leachate after 7.4 BV displacement(4528 mL) were less than 0.1 mg L^{-1}, thus suggesting that both anions were adsorbed by the resin. In other words, there was too much resin exchange capacity compared to the amount of anions in 14.8 BV of the percolating solution.

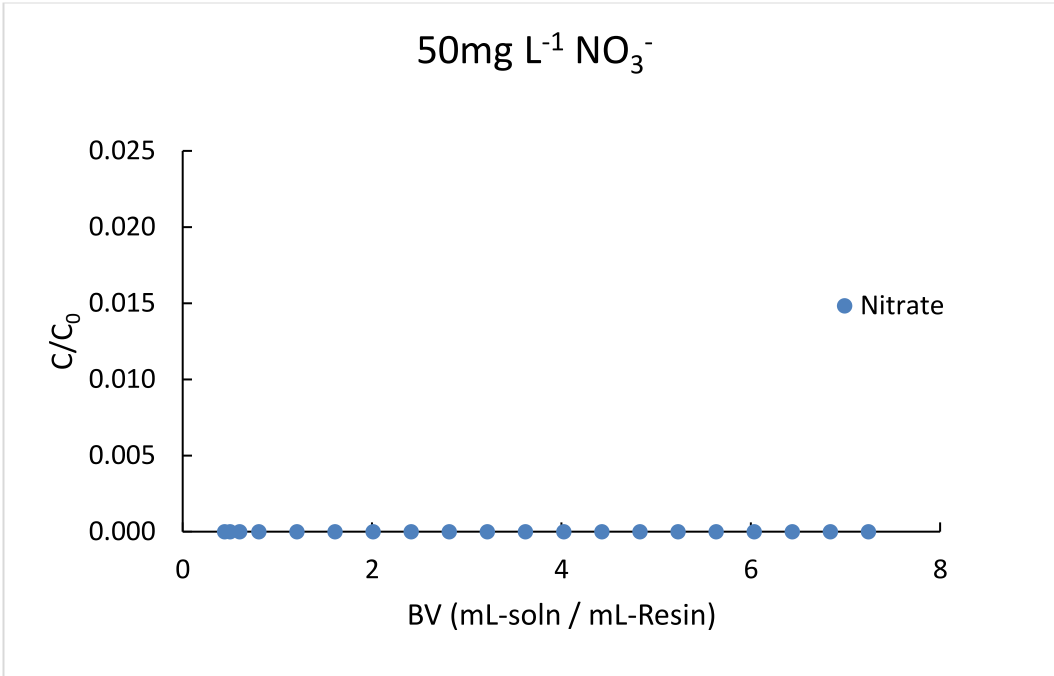

Figure 17: Relative concentration of NO_3^- in the leachate as a function of bed volume. NO_3^- concentration in the percolating solution was 50 mg L^{-1} and the bed volume of the resin corresponded to 612 mL.

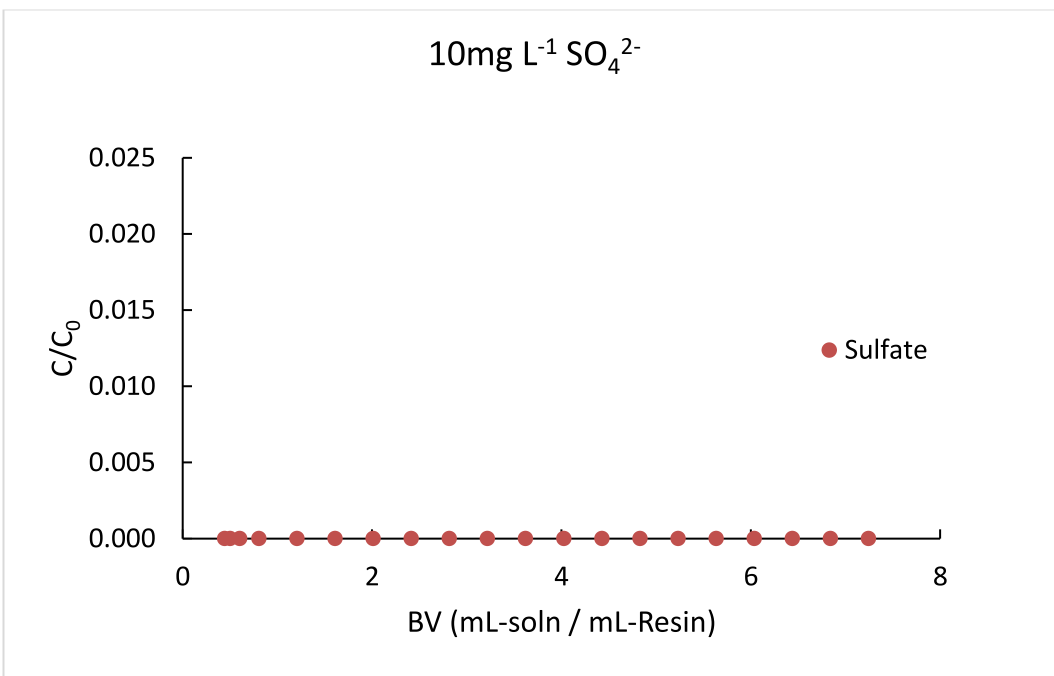

Figure 18: Relative concentration of SO_4^{2-} in the leachate as a function of bed volume. The leachate curve was obtained from a resin column that was previously leached with 50 mg L^{-1} NO_3^- solution (Fig. 12). SO_4^{2-} concentration in the percolating solution was 10 mg L^{-1}.

The second test involved leaching of 50 mg L^{-1} NO_3-N ($NaNO_3$) plus 10 mg L^{-1} SO_4-S (K_2SO_4) solution simultaneously through a resin column. This test was designed to assess if there is any interference in NO_3^- adsorption by SO_4^{2-} ions. For this test also the same amount (612 mL) of new resin was used as in the first test. In Figure 19 are the plots of the relative concentration of NO_3^- and SO_4^- in the leachate after 7.4 BV of percolating solution had passed through the cartridge. At about 1 BV SO_4^{2-} concentration in the leachate increased to 0.6 mg L^{-1}, then returned back to 0 mg L^{-1} at 2 BV. At 6.5 BV both SO_4^- and NO_3^- increased from 0 mg L^{-1} to 2.9 mg L^{-1} and 1.3 mg L^{-1}, respectively. Again, this test showed that the resin was essentially retaining almost all of NO_3^-, and SO_4^{2-} from the percolating solution. In other words, the total resin exchange capacity in the cartridge was too high (too much resin) relative to the amount of NO_3^-, and SO_4^{2-} in the percolating solution. These tests led to the second set of leaching studies with a smaller amount of resin in a syringe tube setting.

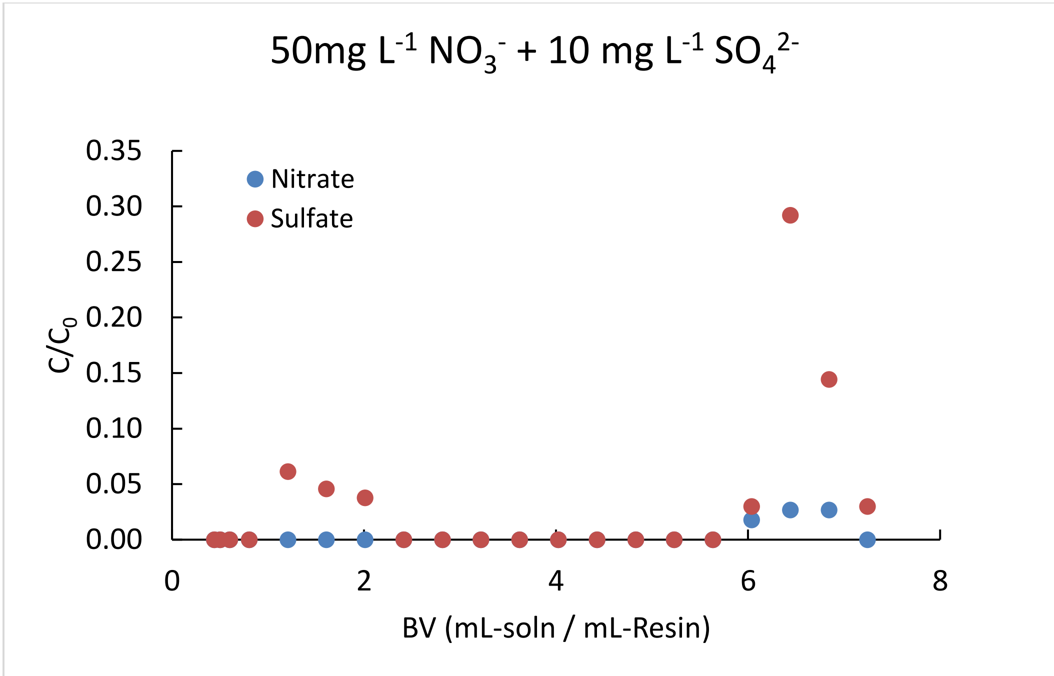

Figure 19: Relative concentration of NO_3^- and SO_4^- in the leachate as a function of bed volume during simultaneous leaching of both anions through the resin column. The leachate curve was obtained from a resin column that had been previously leached with 50 mg L^{-1} NO_3^- solution (Fig. 13). The NO_3^- and SO_4^{2-} concentrations in the percolating solution were 50 mg L^{-1} of NO_3^-+ 10 mg L^{-1} of SO_4^{2}.

In the second laboratory study, 0.5 mL of wet resin was packed into a 3 mL syringe (7 mm diameter) and then eluted with 1,000 mL of 100 mg L^{-1} NO_3^- solution (Figure 20). The leachate curve showed that NO_3^- concentration in the first leachate sample was zero because it was the DI water (used to initially saturate the resin column) that came out of the column. In the second leachate sample, NO_3^--N concentration was 12.1 mg L^{-1} (53.6 mg L^{-1} NO_3^-) and this continuously increased to 21.4 mg L^{-1} NO_3^--N (94.7 mg L^{-1} NO_3^-) at 3400 BV. It appears that a substantial volume of percolating solution by-passed the resin as a side wall flow. In other words, a small part of the percolating solution never reacted with the resin due to the small thickness of resin (0.5 mL) in the syringe. Although the above laboratory tests were incomplete in testing the interference of SO_4^{2-} in adsorption of NO_3^- by the resin, all three tests showed a strong ability of the resin to adsorb anions especially NO_3^- from the percolating solution.

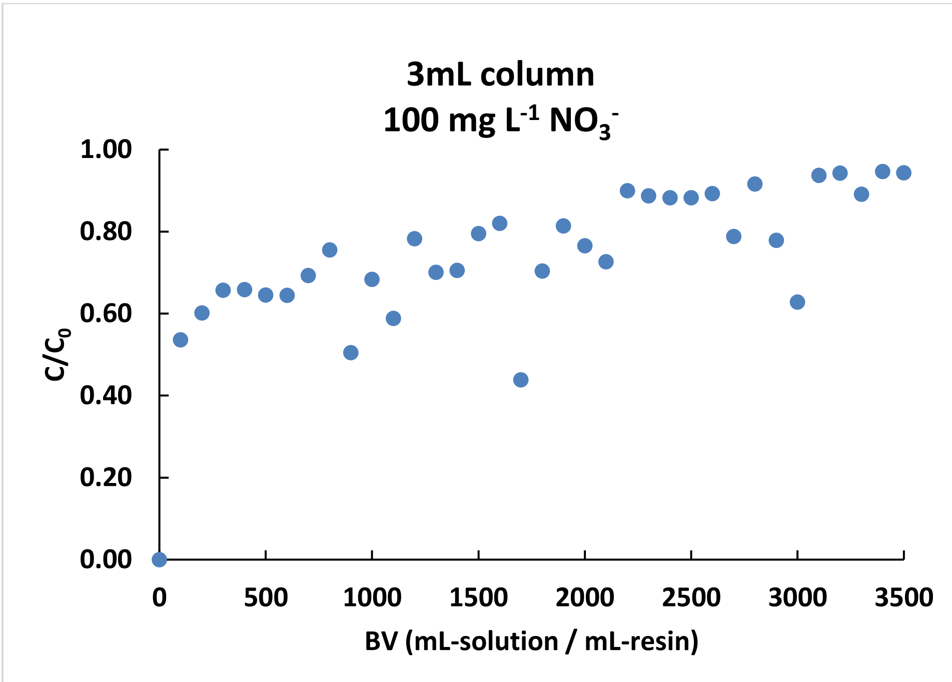

Figure 20: Relative concentration of NO_3^- in the leachate as a function of bed volume when 100 mg L^{-1} of the NO_3^- solution was passed through 0.5 mL of wet resin.

Batch Adsorption Tests

Isotherm adsorption studies with 2 grams of resin showed that NO_3^- and SO_4^{2-} levels remaining in the solution were < 1mg L^{-1} thus indicating a near complete removal (adsorption) of both anions by the resin from the equilibrium solution (Table 1.B, 2.B). In other words, 2 g of resin had too much of retention capacity than the amount of NO_3^- and SO_4^{2-} supplied in the equilibrium solution. Because of the difficulty of identifying an equilibrium concentration in this batch test, a second adsorption isotherm test was conducted with a smaller amount of resin (0.05 g) and a wider range of solution concentrations.

Figure 21 shows the relationship between the NO_3^- concentration adsorbed on the resin and the corresponding concentration in solution at equilibrium in the second batch test. We used the Langmuir adsorption isotherm model (Eq. 1) to fit the data and develop the resin adsorption isotherm for NO_3^-. The slope and intercept of the plot 1/q vs. $1/C_e$ (Figure 1.C) were used to calculate the S_{max} and K_L constant in Eq. 1 (Table 6). The best-fit adsorption isotherm shows that the maximum sorption (S_{max}) of this resin for NO_3^- was 113.6 mg g^{-1} and the binding strength (b) of the resin was 0.09 L mg^{-1}.

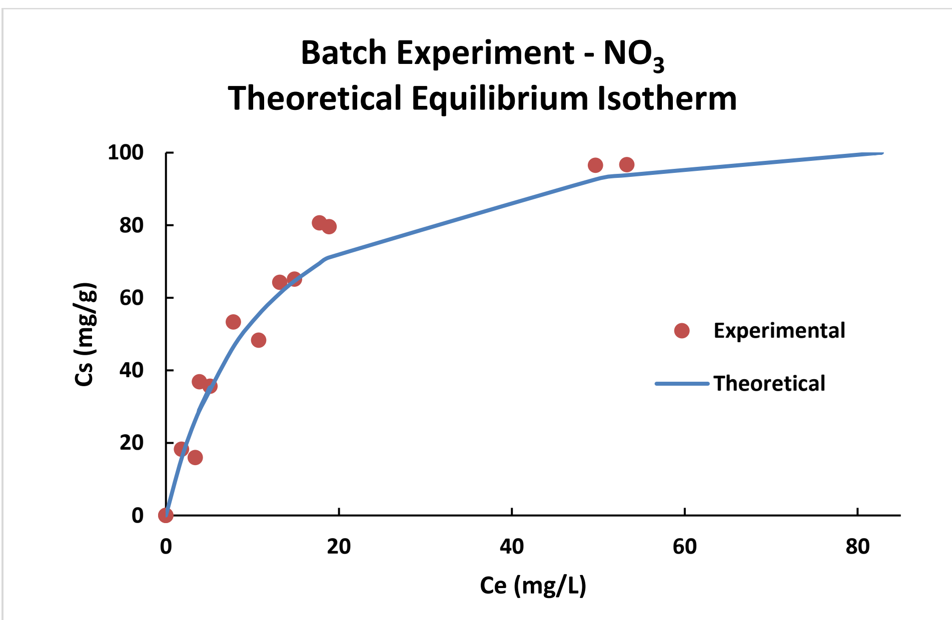

Figure 21: Langmuir adsorption isotherm plot (C_s vs. Ce) for NO_3^- retention by A-32 resin. C_s is the concentration of NO_3^- adsorbed on the resin and Ce is the concentration of NO_3^- in the solution.

Table 6: Values of the parameters in the Langmuir equation.

	S_{max} (mg g^{-1}-dry resin)	K_L (L mg^{-1})
TULSION A-32®	113.6	0.09

DISCUSSION AND CONCLUSIONS

Overall, the resin was very efficient at removing NO_3^- from tile water in the field because of its instantaneous retention properties. Results also showed no presence of heavy metals that would raise concerns about the potential of recycling leachate waste as KNO_3 fertilizer back on the land. Although very effective, in the field it had challenges, such as (1) sediment contamination, (2) interference of other anions, (3) high volume of water outflow, and (4) labor-intensive nature of this technology and our set-ups.

Four of the six columns made it through the two growing seasons from 2015 to 2016. Two of the columns were ruined by the presence of soil particles in tile water from the cracked tile line. The soil in the tile water clogged up the resin in the column thus effectively reducing the percolation rate to very minimal. Sulfate and organic carbon in tile water also interfered with the effectiveness of the resin by blocking the adsorption sites and thus reducing NO_3^- adsorption. The column percolation rates were too low relative to tile water flow rates especially at high rain events, thus effectively reducing the volume of tile water that could be remediated. In other words, the flow rates through the resin columns were too small for the quantity of tile water and thus there was always overflowing.

Lastly, the columns were replaced at least once a week, which meant transporting the columns back and forth to be recharged at least 4 times a month. Although this constraint was solved through the use of flatbed set-up, it required someone to visit the site every day and recharge the resin. Because of the increased volume of tile water passing through a flatbed set-up the capacity of the resin to remove NO_3^- appeared to run out much faster than the column method. There is still much more research needed to understand the effects of having a flatbed set-up over the column set-up. Although flatbed approach can be scaled up through a box (cubic meter resin) type approach and minimize labor need, this may present additional requirements such as a greater fall between the tile and base of the resin box. Also, it will require more water for its recharge and washing as well as some mechanical means to lift and replace the resin box in place.

The adsorption process followed the Langmuir isotherm in the batch sorption studies. There were some difficulties in optimizing the amount of resin and the size of the column to obtained optimum leaching/breakthrough curves. In large cartridges, there was too much resin for the amount of nitrate input in the percolating solution. However, for a small syringe set-up, there was some side flow that never reached the full adsorption and then a breakthrough. However, all the laboratory studies showed that the resin was effective in adsorbing nitrate and sulfate. There is still more work to be done to assess the efficiency of the resin in lab settings and how the other anions interfere with the resin sorption sites.

Feasibility of Using Anion Resin to Remediate Tile Water

The best way to minimize N losses from agricultural land is to optimize the use of N-fertilizer consistent with the weather conditions, the need of the crop, and the potential availability of N from soil organic matter. Since it is difficult to forecast the weather on a long-term basis and it is difficult to predict N mineralization, there will always be some N leaching from agricultural landscapes especially if they are tile drained and there is more precipitation over and above what is needed for evapotranspiration. Considering that there has been a recent trend in increasing rainfall in the Midwestern United States and even more adoption of tile drainage, this even further accentuates the potential of higher N losses from agricultural fields. The impact of higher rainfall and tile drainage is well documented by ever increasing hypoxic zone in the Gulf of Mexico. The long-term average hypoxic zone in the Gulf of Mexico is 14,000 km^2 (EPA, 2015). In 2017, this area was as large as 22,720 km^2. Since passive field technologies like bioreactors, controlled drainage, wetlands, saturated buffers, and cover crops require a residence time of several hours to days, the use of industrial anion resin with instantaneous adsorption provides another alternative to remediate tile water. Then the question is: what are the limitations of its use directly in the field where farmers or local water company can manage recharging of the used resin columns and replace it with recharged columns? Field and laboratory experiments in this study showed several potential limitations of its direct use in the field:

1. The potential presence of sediment in the tile water either from cracked drain tiles or from the presence of surface inlets in the field. Sediment in tile water will clog and foul up the resin thus slowing tile water percolation through the resin. A potential remedy may be to set-up a sediment trap in line before the tile water

reaches the resin column.

2. Presence of SO_4^{2-}, HCO_3^-, and organic anions in tile water that will interfere with the adsorption of NO_3^- by the resin thus reducing its efficiency. Most soils in the Minnesota River Basin are calcareous as well as high in S and organic matter content, which means tile water will always contain SO_4^{2-} and HCO_3^- and organic anions. Potentially, methods can be developed using coagulants to remove sulfate, bicarbonates, and organic anions before the tile water reaches the resin column.
3. Need for timely replacement of used resin column with recharged columns. Since the anion adsorption process is instantaneous thus capturing most of the NO_3^- and other anions in tile water, this also means that columns will need to be replaced with recharged columns rather quickly otherwise continuous addition of high valence anion like SO_4^{2-} that will displace adsorbed NO_3^- from the resin column thus further lowering its efficiency.
4. Since the quantity of water leaving from tile-drained fields is rather large especially early spring, this means a large number of small columns or several bigger resin columns like a 1 m^3 will be needed to capture most of the NO_3^- from tile water. However, this does present a problem of situating these columns in the field because most tiles empty into ditches, which are generally not easily accessible. Furthermore, a large quantity of resin will be expensive. In addition, moving the used and recharged columns back and forth to recharging facilities will be time consuming and expensive.

5. Because of the capture of SO_4^{2-} and organic anions by the resin, a thorough cleaning of the resin will be needed every so often to maintain its efficiency for NO_3^- adsorption.
6. Although the use of muriate of potash (KCl) instead of common salt (NaCl) for recharging resin columns is beneficial in capturing NO_3^- and then recycling it back to the land as fertilizer (KNO_3), muriate of potash (KCl) ($0.38 per gram) is much more expensive than common salt ($0.16 per gram).
7. Recharging and cleaning process requires a substantial amount of clean water and generally this water is not available right next to where drain tiles empty into ditches. Again, this means the resin columns will need to be brought back to the farm or some other facility for recharging. This means additional labor and moving costs. One possible remedy for issues dealing with back and forth movement of used columns and recharged columns may be to build a common NO_3^- remediating facility like that of water works where most of the remediation process can be automated for tile water that is coming from many different fields. However, this will be an expensive set-up.

In spite of the challenges in the use of this resin under field conditions, the results of this study do point out the potential use of this resin in remediating water in individual homes in rural settings where groundwater may be high in NO_3 concentrations.

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APPENDIX A

Table 1.A: Regression analysis on FWNC with the addition of Fertilizer data from 1987-2001 supplied by Ruddy et al., 2006 for the Des Moines River. Fertilizer was not significant in the regression

Regression Statistics	
R Square	0.591380961
Standard Error	2.316807738
Observations	15

	Coefficients	*Standard Error*	*P-value*
Intercept	-20.95783919	14.13784659	0.176519563
PPT	0.006879712	0.003839255	0.110910517
P1	0.003427384	0.003868454	0.401473346
P2	-0.005215685	0.003891277	0.216947199
SB	2.01105E-05	2.04477E-05	0.354163174
PYSB	3.50769E-05	2.08848E-05	0.131559687
FERT	-2.96261E-05	3.50199E-05	0.422145645

Table 2.A: Regression analysis on Ln(N-load) with the addition of Fertilizer data from 1987-2001 supplied by Ruddy et al., 2006 for the Des Moines River. Fertilizer was not significant in the regression

Regression Statistics	
R Square	0.82571142
Standard Error	0.651567513
Observations	15

	Coefficients	*Standard Error*	*t Stat*	*P-value*
Intercept	-2.797847932	3.976057827	-0.70367385	0.501599589
PPT	0.004679421	0.001079733	4.333869464	0.002498924
P1	0.002439111	0.001087945	2.241943829	0.055257597
P2	-0.000536695	0.001094363	-0.49041787	0.637005355
SB	8.58528E-06	5.75062E-06	1.492931321	0.173803863
PYSB	1.00831E-05	5.87354E-06	1.716703748	0.124365718
FERT	-1.33661E-05	9.84882E-06	-1.35713086	0.211786305

Table 3.A: Regression analysis on FWNC with the addition of Fertilizer data from 1987-2001 supplied by Ruddy et al., 2006 for the Iowa River. Fertilizer was not significant in the regression

Regression Statistics	
R Square	0.435707922
Standard Error	1.245338763
Observations	15

	Coefficients	*Standard Error*	*t Stat*	*P-value*
Intercept	1.642545619	6.11298867	0.268698	0.79422
PPT	0.001358829	0.001814994	0.748669	0.473168
P1	-0.000739899	0.001787748	-0.413872	0.688657
SB	3.49374E-06	7.24834E-06	0.482006	0.641307
PYSB	3.00356E-06	6.63533E-06	0.452661	0.661507
FERT	-2.94515E-05	2.70749E-05	-1.087778	0.304964

Table 4.A: Regression analysis on Ln(N-load) with the addition of Fertilizer data from 1987-2001 supplied by Ruddy et al., 2006 for the Iowa River. Fertilizer was not significant in the regression

Regression Statistics	
R Square	0.841942653
Standard Error	0.460028677
Observations	15

	Coefficients	*Standard Error*	*t Stat*	*P-value*
Intercept	-3.953929897	2.258140654	-1.7509671	0.1138703
PPT	0.003708693	0.00067046	5.5315687	0.000365
P1	0.001342901	0.000660395	2.03348123	0.0725253
SB	2.96784E-06	2.67754E-06	1.10842062	0.2964205
PYSB	-8.69569E-07	2.45109E-06	-0.3547675	0.7309349
FERT	-9.83611E-06	1.00015E-05	-0.9834644	0.3510767

Table 5.A: Regression analysis on FWNC with the addition of Fertilizer data from 1987-2001 supplied by Ruddy et al., 2006 for the Raccoon River. Fertilizer was not significant in the regression.

Regression Statistics	
R Square	0.575898058
Standard Error	2.09189796
Observations	15

	Coefficients	*Standard Error*	*t Stat*	*P-value*
Intercept	-16.79692895	12.94017533	-1.29804	0.226549
PPT	0.008213377	0.003772469	2.177189	0.057437
P1	0.002808066	0.003361116	0.835456	0.425083
P2	-0.002943524	0.003587988	-0.82038	0.433188
SB	9.97508E-05	5.08841E-05	1.960355	0.081598
FERT	-1.43475E-05	2.28628E-05	-0.62755	0.545891

Table 6.A: Regression analysis on Ln(N load) with the addition of Fertilizer data from 1987-2001 supplied by Ruddy et al., 2006 for the Raccoon River. Fertilizer was not significant in the regression.

Regression Statistics	
R Square	0.791840419
Standard Error	0.623200192
Observations	15

	Coefficients	*Standard Error*	*t Stat*	*P-value*
Intercept	0.900605163	3.85502539	0.233618478	0.82050838
PPT	0.005372943	0.001123861	4.78078737	0.00100017
P1	0.001216626	0.001001315	1.215028562	0.25526802
P2	-0.000678144	0.001068903	-0.634429909	0.54158894
SB	2.64953E-05	1.51589E-05	1.747830713	0.11443359
FERT	-6.79068E-06	6.81108E-06	-0.997005295	0.34481081

APPENDIX B

Table 1.B: Ion chromatography results from NO3 analysis absorption isotherms

Sample Number	Initial Conc mg NO_3^--N / L	Nitrate-N mg NO_3^--N / L	Nitrate-N mg	Nitrate-N mg leached	Nitrate-N mg adsorbed	Nitrate-N q
1	0	0.00	0.0	0.00	0.00	0.0
2	0	0.00	0.0	0.00	0.00	0.0
3	5	0.00	0.3	0.00	0.25	0.01
4	5	0.00	0.3	0.00	0.25	0.01
5	10	0.00	0.5	0.00	0.50	0.01
6	10	0.00	0.5	0.00	0.50	0.01
7	25	0.00	1.3	0.00	1.25	0.03
8	25	0.00	1.3	0.00	1.25	0.03
9	50	0.00	2.5	0.00	2.50	0.05
10	50	0.00	2.5	0.00	2.50	0.05
11	100	0.00	5.0	0.00	5.00	0.10
12	100	0.00	5.0	0.00	5.00	0.10

Table 2.A: Ion chromatography results from SO_4^{2-} analysis absorption isotherms

Sulfate-S mg SO_4^{2-}-S / l	Sulfate-S mg SO_4^{2-}-S / l	Sulfate-S mg	Sulfate-S mg leached	Sulfate-S mg adsorbed	Sulfate-S q	Sulfate-S 1/q	Sulfate-S 1/C	Sulfate-S Ce/Qe
0.0	0.2	0.0	0.01	0.00	0.0	0.0	5.00	0.0
0.0	0.2	0.0	0.01	0.00	0.0	0.0	4.40	0.0
5.0	0.3	0.3	0.01	0.24	0.00	210.6	3.98	0.02
5.0	0.3	0.3	0.01	0.24	0.00	210.6	3.96	0.02
10.0	0.2	0.5	0.01	0.49	0.01	101.9	5.26	0.05
10.0	0.2	0.5	0.01	0.49	0.01	102.1	4.98	0.05
25.0	0.3	1.3	0.02	1.23	0.02	40.6	2.92	0.07
25.0	0.3	1.3	0.01	1.24	0.02	40.5	3.37	0.08
50.0	0.2	2.5	0.01	2.49	0.05	20.1	5.68	0.28
50.0	0.2	2.5	0.01	2.49	0.05	20.1	5.41	0.27
100.0	0.2	5.0	0.01	4.99	0.10	10.0	5.47	0.55
100.0	0.2	5.0	0.01	4.99	0.10	10.0	5.00	0.50

APPENDIX C

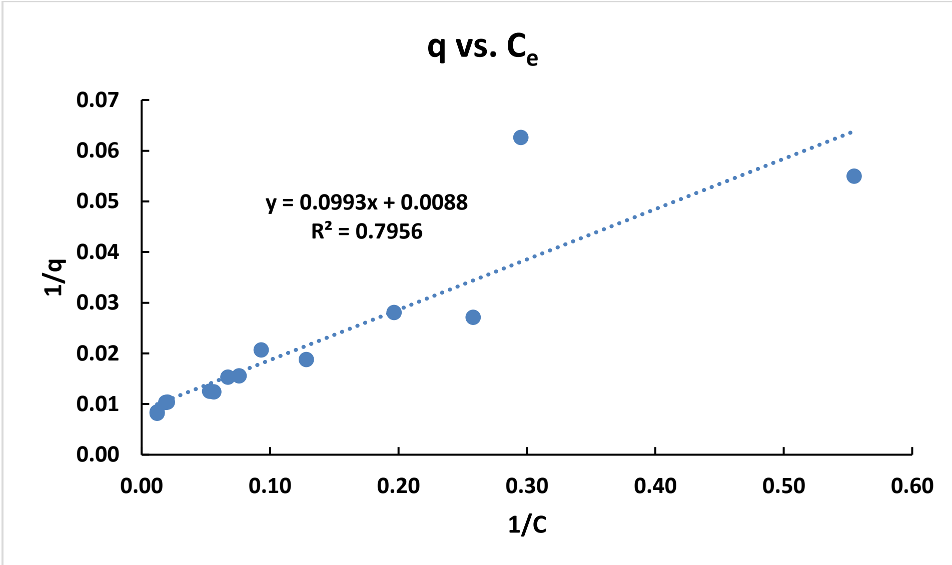

Figure 1.C: Linearization of Langmuir Adsorption Isotherm equation

APPENDIX D

Table 1.D: Flatbed recharge station nitrate concentrations from July 1st to July 4th, 2016. Sample Types indicate where the sample was taken from where T = tile, S1 = sample taken before recharge, R = recharge, W1 = first wash, W2 = second wash, W3 = third wash, and S2 = sample taken after recharging the resin and placing it back under the tile outlet.

July 1st		July 2nd		July 3rd		July 4th	
Sample Type	NO_3-N (mg L^{-1})	Sample Type	NO_3-N (mg L^{-1})	Sample Type	NO_3-N (mg L^{-1})	Sample Type	NO_3-N (mg L^{-1})
T	15.6	T	20.7	T	20.1	T	19.2
S1	18.8	S1	17.5	S1	16.1	S1	14.4
R	21883.3	R	17793.6	R	12524.6	R	6323.2
W1	2682.4	W1	3616.7	W1	4573.9	W1	3468.3
W2	79.2	W2	68.9	W2	776.8	W2	1279.3
W3	28.9	W3	65.5	W3	136.1	W3	148.1
S2	78.7	S2	256.3	S2	611.0	S2	416.3

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